AN ELECTROLYTIC TECHNIQUE TO STUDY THE MOBILITY OF INORGANIC CONSTITUENTS IN SOILS AND WASTE MATERIALS

By

Jennifer Lee Williams

Thesis

Submitted to the Faculty of the

Graduate School of Vanderbilt University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

in

Environmental Engineering

August, 2006

Nashville, Tennessee

Approved:

Professor Florence Sanchez

Professor David S. Kosson

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Florence Sanchez, for her invaluable assistance and guidance in obtaining this degree. I would also like to thank Rossane DeLapp for running all my samples on the ICP-MS and assisting in my interpretation of the data. Mary Jean Morris was instrumental in ordering all of my supplies for the laboratory, and I sincerely appreciate all her efforts throughout the course of my studies as well. I would like to thank my laboratory and office mate, Aniket Borwankar, for his encouragement and friendship. I would also like to thank Professor David Kosson and Professor Andy Garrabrants.

I would like to thank all my friends and family that encouraged and inspired me throughout this entire process, you all know who you are.

I would especially like to thank my husband, Jeffrey, for his infinite patience and understanding over the last two years.

Funding for this research was provided through Vanderbilt University, Start-up Fund, Department of Civil and Environmental Engineering.

TABLE OF CONTENTS

Chapter

Appendix

LIST OF TABLES

Table Page

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Leaching tests are important laboratory tools that provide a method to determine the leachability and mobility of contaminants in the environment. Leaching test results are typically used to evaluate 1) waste classification as “hazardous” or “non-hazardous”, 2) treatment process effectiveness, 3) site assessment and remediation end points, 4) waste management options, and 5) source terms for risk assessment.

Although a wide variety of leaching tests are available in the literature, the majority address the role of pH and LS, but few address the effect of oxidation/reduction reactions on contaminant release. Reducing conditions have been shown to lead to the mobilization of redox-sensitive inorganic species, such as arsenic, iron, or chromium. These conditions occur in environments that are anoxic or limited in oxygen, which may be due to flooding, microbial activity, or an excess of organic materials.

In the laboratory, reducing conditions have been studied using biological methods, chemical reducing agents, and electrolytic techniques. Biological methods involve the use of microorganisms in order to obtain reducing conditions. This method can take up to several weeks and is dependent upon the growth and maintenance of the microorganisms. Chemical reducing agents involve chemicals to obtain reducing conditions. These chemical agents may react with the system and alter the oxidation/reduction reactions that would normally occur. Electrolytic techniques involve applying an electrolytic potential in order to change the redox of the system. This method eliminates both the use of chemical reducing agents and microorganisms.

The specific objectives of the research presented here were to: 1) develop an apparatus based on electrolytic techniques and 2) use the apparatus to determine the mobility of redox-sensitive species in soils and waste materials over a range of pH and Eh values. These objectives were met through two sets of studies: 1) preliminary studies using sampled-current voltammetry experiments consisting of cyclic potential sweeps and 2) electrolytic oxidation/reduction studies. The objectives of the preliminary studies were to determine the effects of different salt bridges, working electrodes, and iron souces on the Eh, pH, and Faradic current of the electrolytic cell. The objectives of the electrolytic oxidation/reduction studies were to determine the effect of time and varying applied potential on changes in suspension pH, Eh, and constituent mobility. Three different systems were used: 1) an iron(III) nitrate solution (test system), 2) an arsenic contaminated soil suspension (naturally oxidized system), and 3) a furnace slag suspension (naturally reduced system).

Chapter II provides a literature review of reducing conditions and leaching in the natural environment. Information on the different types of leaching tests that are currently in use, the effect of oxidation/reduction reactions on the mobility of arsenic and iron is presented, and the laboratory methods that have been used to characterize these reactions (i.e. biological techniques, chemical reducing agent techniques, and electrolytic techniques) are discussed. Chapter III provides the experimental design and describes the materials and methods used in this research. Chapter IV presents the results and provides discussion. Finally, chapter V presents the conclusions and recommendations.

CHAPTER II

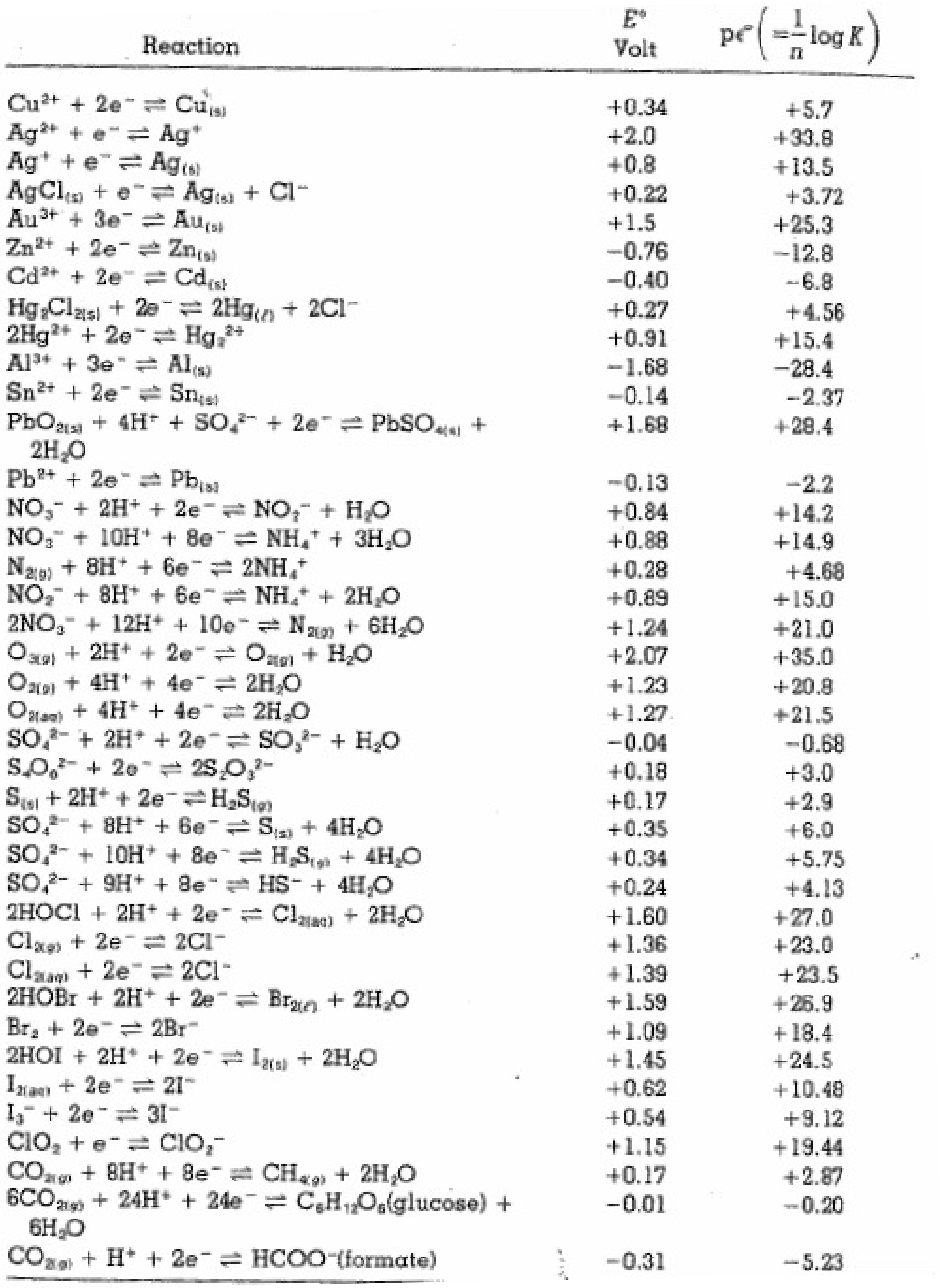
LITERATURE REVIEW

Reducing Conditions in the Environment

The status of an environment as “oxidizing” or “reducing” is related to the amount of oxygen that is present in the environment. In oxic systems, oxygen acts as an electron receptor or oxidizing agent; therefore, when oxygen is low or absent, the system will become more electron rich or reducing (Bohn et al., 1985).

Reduction is due to the transfer of electrons between chemical species that exist in an environment, and is coupled to an oxidation reaction. Reduction involves the acceptance of an electron from a donor that is, itself, being oxidized. Reduction and oxidation reactions will therefore form chemical species of different oxidation states (Ollier, 1984).

The stability of an element’s oxidation state is related to the energy involved in adding or removing electrons, which is expressed as a standard reduction potential (E°) (Ollier, 1984). A typical convention for E° is to present the half-reaction with the reduced species on the right. The E° of different elements is determined relative to the ease that hydrogen ions may accept electrons to form hydrogen gas, which has been given an E° of 0.00V (Bland et al., 1998). A short list of reduction potentials is presented in Figure 1.



Reaction	$E°$ Volt	$p\epsilon°\left(=\frac{1}{n}\log K\right)$
$Cu^{2+} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34	+5.7
$Ag^{2+} + e^- \rightleftharpoons Ag^+$	+2.0	+33.8
$Ag^+ + e^- \rightleftharpoons Ag_{(s)}$	+0.8	+13.5
$AgCl_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Cl^-$	+0.22	+3.72
$Au^{3+} + 3e^- \rightleftharpoons Au_{(s)}$	+1.5	+25.3
$Zn^{2+} + 2e^- \rightleftharpoons Zn_{(s)}$	−0.76	−12.8
$Cd^{2+} + 2e^- \rightleftharpoons Cd_{(s)}$	−0.40	−6.8
$Hg_2Cl_{2(s)} + 2e^- \rightleftharpoons 2Hg_{(\ell)} + 2Cl^-$	+0.27	+4.56
$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+0.91	+15.4
$Al^{3+} + 3e^- \rightleftharpoons Al_{(s)}$	−1.68	−28.4
$Sn^{2+} + 2e^- \rightleftharpoons Sn_{(s)}$	−0.14	−2.37
$PbO_{2(s)} + 4H^+ + SO_4^{2-} + 2e^- \rightleftharpoons PbSO_{4(s)} + 2H_2O$	+1.68	+28.4
$Pb^{2+} + 2e^- \rightleftharpoons Pb_{(s)}$	−0.13	−2.2
$NO_3^- + 2H^+ + 2e^- \rightleftharpoons NO_2^- + H_2O$	+0.84	+14.2
$NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$	+0.88	+14.9
$N_{2(g)} + 8H^+ + 6e^- \rightleftharpoons 2NH_4^+$	+0.28	+4.68
$NO_2^- + 8H^+ + 6e^- \rightleftharpoons NH_4^+ + 2H_2O$	+0.89	+15.0
$2NO_3^- + 12H^+ + 10e^- \rightleftharpoons N_{2(g)} + 6H_2O$	+1.24	+21.0
$O_{3(g)} + 2H^+ + 2e^- \rightleftharpoons O_{2(g)} + H_2O$	+2.07	+35.0
$O_{2(g)} + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23	+20.8
$O_{2(aq)} + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.27	+21.5
$SO_4^{2-} + 2H^+ + 2e^- \rightleftharpoons SO_3^{2-} + H_2O$	−0.04	−0.68
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.18	+3.0
$S_{(s)} + 2H^+ + 2e^- \rightleftharpoons H_2S_{(g)}$	+0.17	+2.9
$SO_4^{2-} + 8H^+ + 6e^- \rightleftharpoons S_{(s)} + 4H_2O$	+0.35	+6.0
$SO_4^{2-} + 10H^+ + 8e^- \rightleftharpoons H_2S_{(g)} + 4H_2O$	+0.34	+5.75
$SO_4^{2-} + 9H^+ + 8e^- \rightleftharpoons HS^- + 4H_2O$	+0.24	+4.13
$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_{2(aq)} + 2H_2O$	+1.60	+27.0
$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-$	+1.36	+23.0
$Cl_{2(aq)} + 2e^- \rightleftharpoons 2Cl^-$	+1.39	+23.5
$2HOBr + 2H^+ + 2e^- \rightleftharpoons Br_{2(\ell)} + 2H_2O$	+1.59	+26.9
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.09	+18.4
$2HOI + 2H^+ + 2e^- \rightleftharpoons I_{2(s)} + 2H_2O$	+1.45	+24.5
$I_{2(aq)} + 2e^- \rightleftharpoons 2I^-$	+0.62	+10.48
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.54	+9.12
$ClO_2 + e^- \rightleftharpoons ClO_2^-$	+1.15	+19.44
$CO_{2(g)} + 8H^+ + 8e^- \rightleftharpoons CH_{4(g)} + 2H_2O$	+0.17	+2.87
$6CO_{2(g)} + 24H^+ + 24e^- \rightleftharpoons C_6H_{12}O_6$(glucose) $+ 6H_2O$	−0.01	−0.20
$CO_{2(g)} + H^+ + 2e^- \rightleftharpoons HCOO^-$(formate)	−0.31	−5.23

Figure 1. List of reduction potentials for various half reactions (Snoeyink et al., 1980).

In order to determine the reduction potential (Eh) of a redox reaction, the Nernst equation is used. The Nernst equation for the reaction $A + B \Leftrightarrow C + D$ is as follows (Snoeyink et al., 1980):

$$E = E^o + \frac{2.303RT}{nF} \log \frac{[C][D]}{[A][B]} \tag{1}$$

where E° = standard reduction potential (V)

R = gas constant ($\mathrm{JK^{-1}mol^{-1}}$)

F = Faraday's constant (kcal/volt-equivalent)

n = number of electrons involved in the reaction

The standard reduction potential is related to the Gibbs free energy in the following equation (Langmuir, 1997):

$$E^o = \frac{-\Delta G_r^o}{nF} \tag{2}$$

The reduction potential can also be reported as pE, which is the negative common logarithm of the electron concentration (e-), or:

$$pE = -\log_{10}(e^-) \tag{3}$$

The pE is related to Eh by the following equation:

$$pE = \frac{[nF] \cdot Eh}{2.303RT} \tag{4}$$

In the natural environment, the range of Eh is from 1.2 to 0.0V at a pH of 0; whereas at a pH of 14, the range of Eh is from -0.8 to +0.4 V (Ollier, 1984). Outside this range, water will decompose. In soils, a range of +0.3 to +0.8 V corresponds to oxic conditions. A range of -0.4 to +0.1 V correspond to reducing, anaerobic conditions in soils (Alloway, 1995). Generally, a high Eh level corresponds to a low pH value, and conversely, a low Eh level corresponds to a high pH value.

Since Eh measurements are often difficult to obtain and interpret in the environment, Berner's redox classification was developed (Langmuir, 1997). This classification system is based on the amount of dissolved oxygen or dissolved sulfide within an environment, and is broken down into three categories: 1) oxic, 2) suboxic, and 3) anoxic. An oxic environment is considered to have a dissolved oxygen content of greater than 30 μM. A suboxic environment has a dissolved oxygen content between 1 and 30 μM. An anoxic environment has a dissolved oxygen content of less than 1 μM. The anoxic environment can be further subdivided on the basis of dissolved sulfide. A sulfidic environment has greater than 1 μM of dissolved sulfide, whereas a nonsulfidic environment has less than 1 μM.

Reducing conditions can occur in the environment when there is anaerobic activity, flooding of soils, an absence of oxygen, an excess of organic material, or when agricultural practices change soil drainage. Approximately 70% of the earth's surface is considered an oxygen-poor environment due to the presence of water (Bohn et al., 1985). Elements that are affected by redox changes within the environment include the following: C, N, O, S, Fe, Mn, Ag, As, Cr, Cu, Hg, Se, and Pb (Alloway, 1995; Plant et al., 2003). Figure 2 shows the range of Eh-pH values that are found in different areas within the environment.

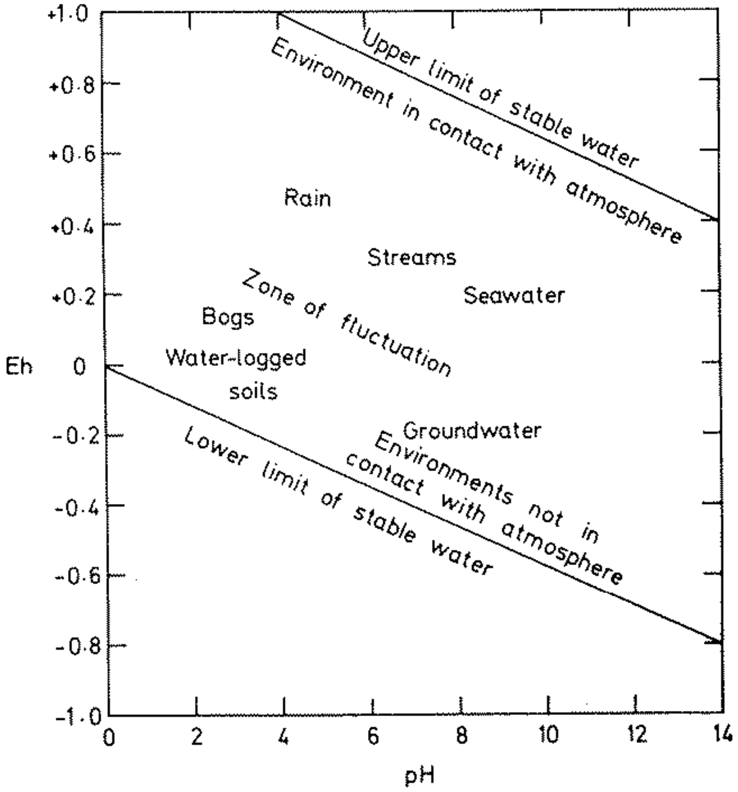


Figure 2. Eh-pH range of the natural environment (Ollier, 1984).

As shown in Figure 2, the environment in contact with the atmosphere is under oxidizing conditions, which is due to the presence of oxygen. As oxygen is limited, due to anaerobic activity or some other depletion of oxygen, such as the water-logging of soils, the environment becomes more reducing. This change from an oxidizing environment to a reducing environment leads to changes in the oxidation state of elements. This is important because the oxidation state of an element imparts certain characteristics that are unique to that oxidation state. In the case of iron, the oxidized form, Fe^{+3}, is less mobile than the reduced form, Fe^{+2}, due to the formation of insoluble iron(III) hydroxides (Datta, 1981). The toxicity of an element may also be affected by the oxidation state, as in the case of arsenic, where the (+5) form is less acutely toxic than the (+3) form (Ng, 2005). Thus, an assessment of constituents under a range of redox conditions is necessary to better understand fate and transport of contaminants in the environment.

A redox ladder is a method of presenting redox couples in order of descending Eh, an example of which is presented in Figure 3. Theoretically, the more oxidizing species, or the ones that appear higher on the ladder, are capable of oxidizing the couples found below. Simultaneously, the reduced couples near the bottom of the ladder will reduce the species with the greater Eh.

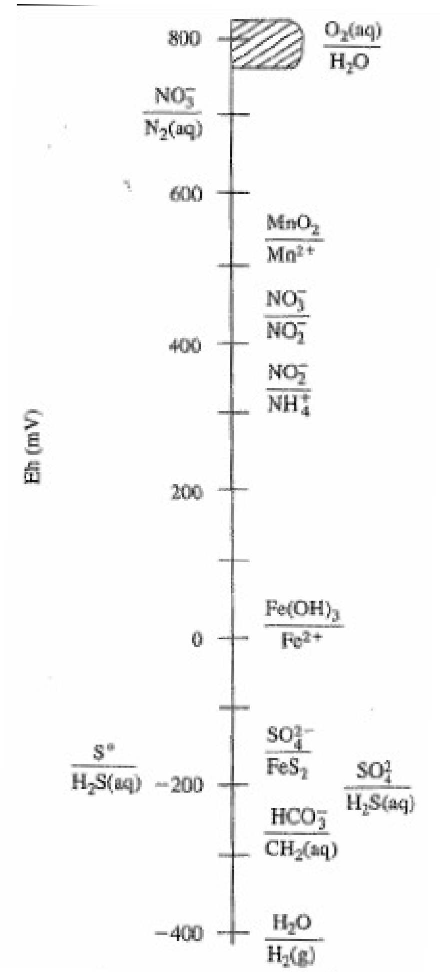


Figure 3. A redox ladder for selected redox couples.

Leaching in the Environment

Leaching is a type of chemical weathering that occurs naturally in the environment. The material undergoing leaching may be a natural source, such as a rock or soil, or an anthropogenic source, such as a building or a waste material. Leaching occurs when a solution (sea water, rain water, groundwater) comes into contact with a material, allowing chemical interactions to occur between the solution and the material. Specifically, the solution provides ions that will come into contact with the material's surface. The ions interact with the material, allowing for chemical reactions such as hydration, hydrolysis, sorption, oxidation-reduction, carbonation, and dissolution to occur during the solution interaction (Pickering, 1989).

The steps that occur when a constituent is dissolved due to leaching are as follows: 1) migration of the reactants from the bulk solution to the surface, 2) adsorption and transfer of reaction species, 3) chemical reactions between the reactants and the material surface, 4) detachment of the reaction products, and 5) transport of reaction products through concentration gradients into the bulk solution.

Dissolution reactions may be diffusion-controlled or surface-controlled. In diffusion-controlled dissolution, the concentration varies in proportion to the square root of time, and dissolution is limited by the rate at which the constituents are transported from the surface of the mineral into the bulk solution. In surface-controlled dissolution, the kinetics follow a zero-order rate law, and are limited by the speed of the reaction occurring at the mineral surface (Stumm et al., 1998). Stability and solubility of the constituents of both the matrix and solution affect the rate at which leaching occurs.

Leaching Tests

Leaching tests consist of contacting solid materials with solutions. Leaching tests are used for 1) the classification of wastes as “hazardous” versus “non-hazardous”, 2) site assessment and remediation end points, 3) treatment process effectiveness, 4) waste management options, and 5) source term evaluation for risk assessment (van der Sloot et al., 2001; Kosson et al., 2002; van der Sloot, 2002).

Three categories of leaching tests exist: 1) tests that simulate constituent release in a specific environmental scenario (e.g. TCLP (EPA, 1992)), 2) tests that use sequential extractions (Tessier et al., 1979), and 3) tests that determine fundamental leaching parameters (Kosson et al., 2002).

Tests that simulate constituent release under specific environmental scenarios have been used to evaluate the mobility of constituents within solid and multi-phase wastes (EPA, 1992). These tests were developed for a specific scenario, but have been used for a wide range of scenarios outside the scope of the original intent of the test. The limitation of these tests are that they have been shown to lead to an underestimation or overestimation of the release of contaminants in the environment (Sanchez et al., 2002; Lim et al., 2004; Jong et al., 2005).

Sequential extraction methods involve the partitioning of the sample into different fractions. For example, the Tessier, Campbell et al. (Tessier et al., 1979) method involves five fractions: 1) the exchangeable fraction, 2) the fraction bound to carbonates, 3) the fraction bound to iron and manganese oxides, 4) the fraction bound to organic matter, and 5) the residual fraction. Extensive research has been done using the sequential extraction methods for analyzing trace metals such as Cd, Co, Cu, Ni, Pb, Zn, Fe, Mn, Si, and As in sediments, soils, and air. The limitations of this method are the 1) nonselectivity of extractants, 2) the redistribution of trace elements among the different phases during extraction, and 3) the difficulty to validate the method (Kheboian et al., 1987; Nirel et al., 1990; Tessier et al., 1991). Also, the operationally defined nature of the procedure limits the ability to generalize the test for use in a management framework (Kosson et al., 2002).

The integrated framework developed by Kosson et al. (Kosson et al., 2002) for leaching is an example of leaching tests that define fundamental leaching parameters, and is described in the next section.

Integrated Framework for Evaluating Leaching (Kosson et al., 2002)

An integrated framework for leaching has been developed to evaluate the leaching of inorganic contaminants in a wide range of waste and secondary materials. This framework is based on the assessment of fundamental leaching parameters, such as pH and liquid-to-solid (LS) ratio. The framework is subdivided into three tiers, with each tier consisting of three testing levels. Tier 1 addresses the availability of the constituent. Tier 2 addresses equilibrium based assessment, and Tier 3 addresses mass-transfer based assessment. A schematic depicting the tiered framework is presented in Figure 4. In association with this framework, a database/expert system integrating the results of different tests has been developed in order to better determine the long-term release of constituents (van der Sloot et al., 2003).

Although the integrated framework takes into consideration the fundamental leaching parameters of pH and LS ratio, oxidation-reduction conditions continue to be an underdeveloped area (van der Sloot, 2005).

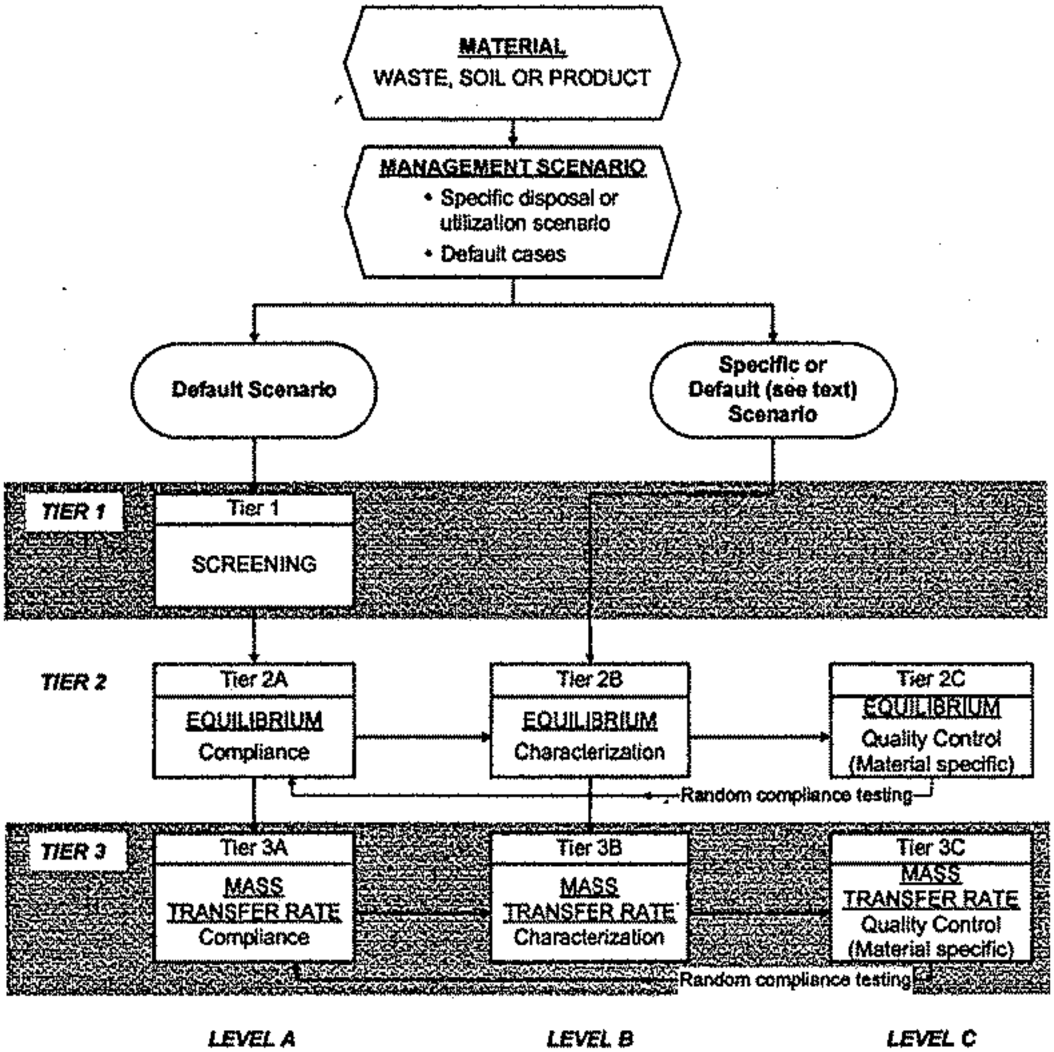
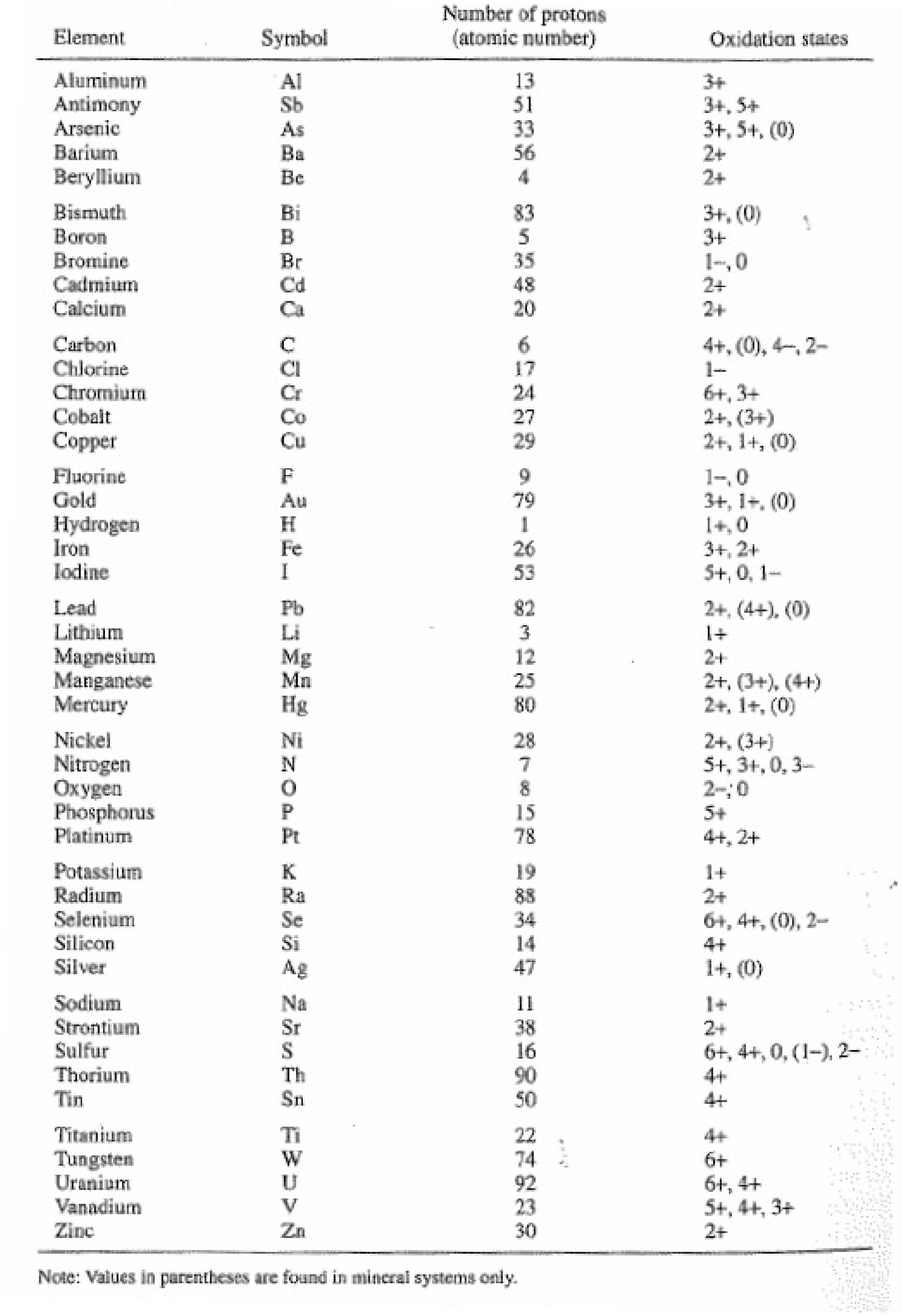


Figure 4. Integrated framework for leaching (Kosson et al., 2002).

Effect of Oxidation/Reduction Conditions on the Mobility of Inorganic Species

As stated previously, elements may exist in the natural environment in multiple oxidation states based on the surrounding environs. The typical macro constituents that undergo redox reactions in the environment include hydrogen, oxygen, sulfur, nitrogen, manganese, and carbon (Langmuir, 1997). The micro constituents that undergo redox reactions within the environment are also of great importance, due to the fact that their toxicity and mobility may be enhanced due to changes in oxidation state, which may ultimately harm biota. A list of typical elements found in the environment and their respective possible oxidation states is presented in Figure 5.

The most stable oxidation states can be presented in graphical form as a function of their Eh and pH. These Eh-pH diagrams are known as Pourbaix diagrams (Pourbaix, 1966). These graphs represent a theoretical determination of the oxidation state that dominates in a specific Eh-pH range in the environment. The boundaries between the different oxidation states are determined to be points where the concentrations of the oxidation state represented on either side of the boundary are equal. The Eh measured in complex natural systems may differ from the Pourbaix diagrams, which were created using dilute, simple systems. This may be due to the kinetics of the redox reactions or the existence of mixed potentials within the environment (Langmuir, 1997).



Element	Symbol	Number of protons (atomic number)	Oxidation states
Aluminum	Al	13	3+
Antimony	Sb	51	3+, 5+
Arsenic	As	33	3+, 5+, (0)
Barium	Ba	56	2+
Beryllium	Be	4	2+
Bismuth	Bi	83	3+, (0)
Boron	B	5	3+
Bromine	Br	35	1–, 0
Cadmium	Cd	48	2+
Calcium	Ca	20	2+
Carbon	C	6	4+, (0), 4–, 2–
Chlorine	Cl	17	1–
Chromium	Cr	24	6+, 3+
Cobalt	Co	27	2+, (3+)
Copper	Cu	29	2+, 1+, (0)
Fluorine	F	9	1–, 0
Gold	Au	79	3+, 1+, (0)
Hydrogen	H	1	1+, 0
Iron	Fe	26	3+, 2+
Iodine	I	53	5+, 0, 1–
Lead	Pb	82	2+, (4+), (0)
Lithium	Li	3	1+
Magnesium	Mg	12	2+
Manganese	Mn	25	2+, (3+), (4+)
Mercury	Hg	80	2+, 1+, (0)
Nickel	Ni	28	2+, (3+)
Nitrogen	N	7	5+, 3+, 0, 3–
Oxygen	O	8	2–, 0
Phosphorus	P	15	5+
Platinum	Pt	78	4+, 2+
Potassium	K	19	1+
Radium	Ra	88	2+
Selenium	Se	34	6+, 4+, (0), 2–
Silicon	Si	14	4+
Silver	Ag	47	1+, (0)
Sodium	Na	11	1+
Strontium	Sr	38	2+
Sulfur	S	16	6+, 4+, 0, (1–), 2–
Thorium	Th	90	4+
Tin	Sn	50	4+
Titanium	Ti	22	4+
Tungsten	W	74	6+
Uranium	U	92	6+, 4+
Vanadium	V	23	5+, 4+, 3+
Zinc	Zn	30	2+

Note: Values in parentheses are found in mineral systems only.

Figure 5. Oxidation states of selected elements in the environment (Langmuir, 1997).

Arsenic Redox Chemistry and Mobility

Arsenic is a metalloid that is the 20th most abundant element in the Earth's crust at 1.5-2 ppm, and is found naturally in the environment in bodies of water and soils (1977). In industry, smelters, gold mines, arsenic-containing coal and waste sites are anthropogenic sources resulting in the increased levels of arsenic that are often found in the environment. Both natural and anthropogenic sources of arsenic pose problems to humans, and chronic toxicity has become a serious medical issue around the globe. For instance, approximately 50 million people in Bangladesh and 6 million people in China are exposed to drinking water containing greater than 50 μg/L of arsenic (1977; Frankenberger, 2002; Plant et al., 2003).

The Eh-pH diagram for arsenic is shown in Figure 7. The diagram shows that at equilibrium, $H_3AsO_4^{\circ}$, $H_2AsO_4^{3-}$, $HAsO_4^{2-}$, AsO_4^{3-}, $HAsO_2$, and the solids As_2O_3 and As are theoretically the dominant species; however, the natural environment may not be under equilibrium conditions. The most prevalent oxidation states of arsenic in soils are As(III) and As(V) (Masscheleyn et al., 1991).

The different oxidation states impart different properties to the constituent, and these oxidation states cycle in the environment, as shown in Figure 6. As(III) has been found to be more toxic and more mobile than the As(V) form (Ferguson et al., 1972; Knowles et al., 1983). Although As(III) is the more mobile form, it has been shown that both As(III) and As(V) can be adsorbed to iron oxide and iron hydroxides (Pierce et al., 1981; Gupta et al., 2005). The As(III) may adsorb directly onto the mineral or may be oxidized rapidly in the presence of the iron oxyhydroxide, allowing it to then adsorb to the surface in the As(V) oxidation state (de Vitre et al., 1991; Manning et al., 1997). Two mechanisms have been proposed for the release of arsenic from its association with iron and aluminum oxides: 1) direct arsenate reduction and 2) indirect arsenate reduction (Frankenberger, 2002). In direct arsenate reduction, the arsenic itself is reduced from As(V) to As(III), which is then released into solution. In indirect arsenate reduction, the substrate is reduced, which releases As(V) into solution that is then subsequently reduced to As(III). A graphical representation of the two mechanisms are presented in Figure 8.

Experiments have shown that bacteria are capable of affecting the speciation of arsenic (Ahmann et al., 1994; Ahmann et al., 1997; Macy et al., 2000; Oremland et al., 2000; Niggemyer et al., 2001; Chatain et al., 2005). Four different groups of organisms that affect the speciation of arsenic have been identified: 1) dissimilatory arsenate-reducing prokaryotes (DARPs) (Newman et al., 1997; Blum et al., 1998; Oremland et al., 2000; Niggemyer et al., 2001), 2) chemoautotrophic arsenite oxidizers (CAOs) (Santini et al., 2000; Oremland et al., 2005; Rhine et al., 2006), 3) heterotrophic arsenite oxidizers (HAOs) (Oremland et al., 2005; Salmassi et al., 2006), and 4) arsenate-resistant microorganisms (Anderson et al., 1992; Macur et al., 2004; Oremland et al., 2005). DARPs are bacteria that respire As(V), reducing it to As(III). CAOs and HAOs gain energy through the oxidation of As(III) to As(V); however, CAOs use carbon dioxide as the terminal electron while HAOs require organic matter. Arsenate reducing bacteria detoxify their cells through the reduction of As(V) to As(III).

The reduction of arsenic may also be coupled to the microbial reduction of iron in the environment. Dissimilatory metal-reducing bacteria, DMRB have been shown to be capable of reducing iron from Fe(III) to Fe(II), which would release into solution any metal that was associated with the oxidized iron (Liu et al., 2002).

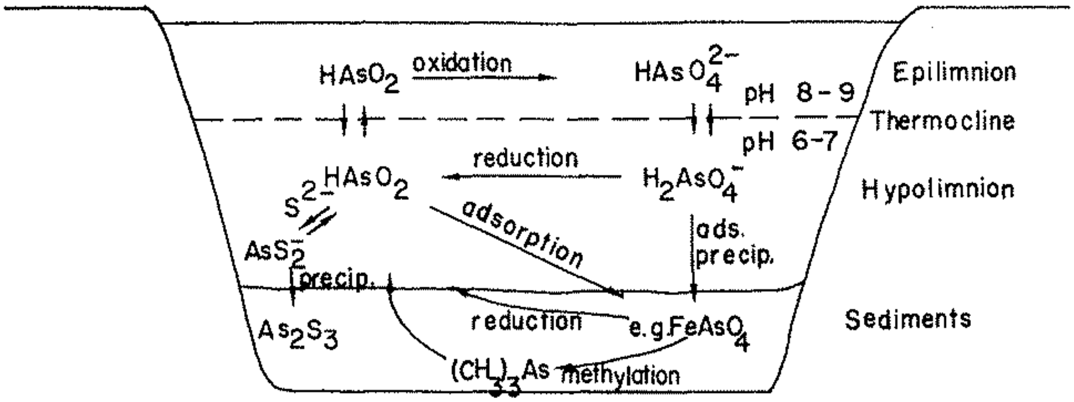


Figure 6. Example of arsenic cycling in a lake (Ferguson et al., 1972).

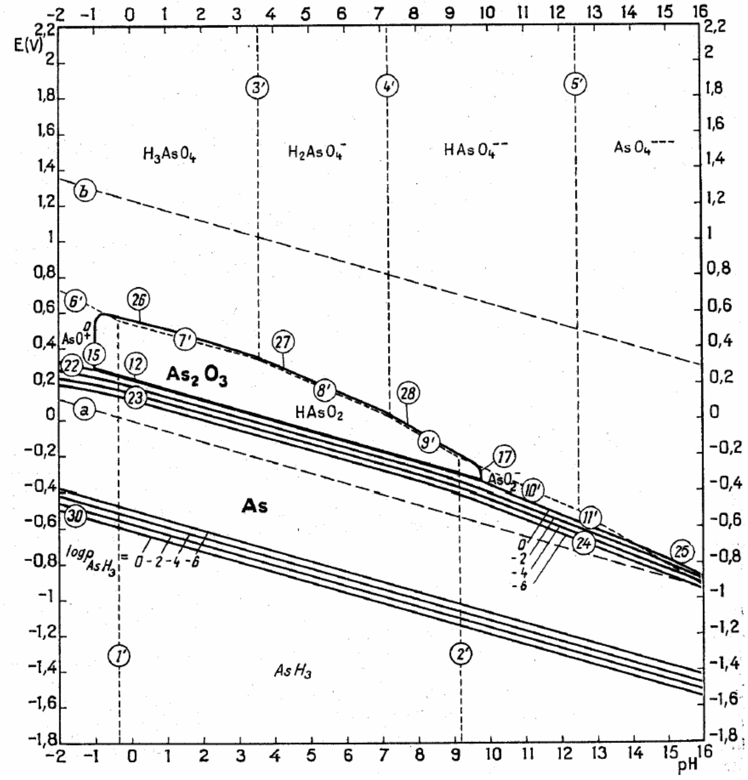


Figure 7. Eh-pH diagram of Arsenic (Pourbaix, 1966).

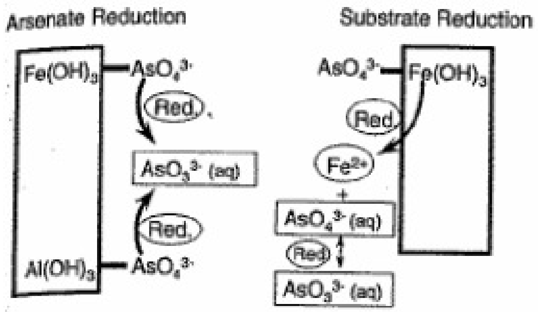


Figure 8. Mechanisms for the reduction of arsenic: 1) arsenate reduction and 2) substrate reduction (Frankenberger, 2002).

Iron Redox Chemistry and Mobility

The Eh-pH diagram for iron is presented in Figure 9. At equilibrium, $Fe(OH)^{2+}$, $Fe(OH)_3$, $FeO4^{2-}$, Fe^{2+}, and Fe can be found in the environment. Typically, Fe^{2+} is found in reducing conditions below a pH of 7. $Fe(OH)_3$ and $Fe(OH)^{2+}$ dominate in oxidizing conditions. As mentioned in the previous section, arsenic, as well as other redox sensitive species, can adsorb to the surface of iron oxyhydroxides, rendering them immobile in the environment (Belzile et al., 1990; de Vitre et al., 1991; Manning et al., 1997). The reduction of iron may also occur due to interactions with DMRB, as mentioned in the section on arsenic (Liu et al., 2002).

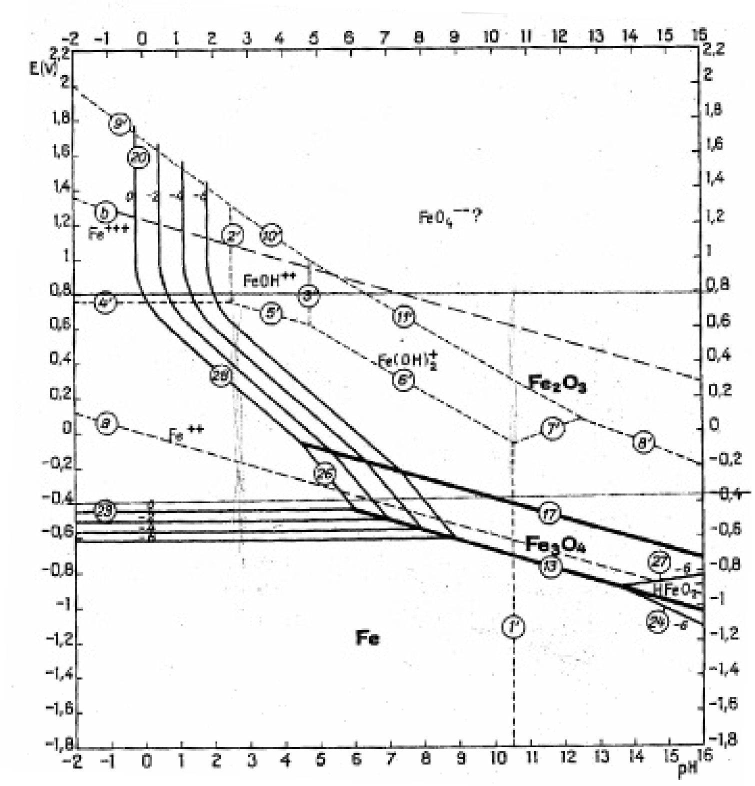


Figure 9. Eh-pH diagram for iron (Pourbaix, 1966).

Laboratory Techniques Used for Constituent Mobility under Reducing Conditions

Laboratory techniques have been developed to understand and replicate reducing conditions occurring in the natural environment in a laboratory setting. Three types of laboratory techniques can be used: 1) biological techniques, 2) chemical reducing agent techniques, and 3) electrolytic techniques.

Biological Techniques

Two types of biological techniques exist: 1) microcosm techniques where the Eh is regulated (Hanke et al., 1943; Patrick et al., 1973; Masscheleyn et al., 1990; Masscheleyn et al., 1991; Guo et al., 1997; Yu et al., 2003) and 2) batch extractions where the Eh is not regulated (Ahmann et al., 1997; Guha, 2004; Islam et al., 2004; Chatain et al., 2005).

An example of the first type of biological techniques (microcosm technique) has been developed by Patrick, et al. (Patrick et al., 1973) to control redox potential from +600 to -250 mV by regulating the amount of oxygen or air introduced to the system. The methodology and apparatus were adapted from previous work where Eh was controlled in order to characterize the limiting conditions for *Cl. tetani* and *Bacteroides vulgatus* (Hanke et al., 1943). In this method, the reducing conditions were created by bacteria and regulated through the addition of oxygen as necessary. This methodology has been employed to study: 1) nitrate reduction in estuarine sediment (Buresh et al., 1981), 2) the effect of redox potential on CO_2, CH_4, and N_2O in rice soils (Yu et al., 2003), 3) phosphogypsum chemistry (Carbonell-Barrachina et al., 2002), 4) the effect of redox potential on arsenic and selenium speciation (Masscheleyn et al., 1990; Masscheleyn et al., 1991), and 5) the effect of sediment redox on heavy metals in estuarine sediment (Guo et al., 1997). A similar microcosm technique has been used to regulate the Eh from +200 to +700 mV using oxygen to increase the Eh or glucose and beech-litter extract to decrease the Eh (Rennert et al., 2005).

The second type of biological techniques (batch extractions) has been used to study the mobilization of arsenic, molybdenum, and iron from soils and sediments using indigenous bacteria (Ahmann et al., 1997; Bennett et al., 2003; Chatain et al., 2005; Davidson et al., 2005). The Hungate technique (Miller et al., 1974), which is a method to handle microbes under strictly anoxic conditions, has been used to cultivate new microbial strains capable of reducing constituents such as arsenic, selenium, and sulfate (Newman et al., 1997; Blum et al., 1998; Oremland et al., 2000; Niggemyer et al., 2001).

These biological techniques are time intensive (requiring incubation time of two months or more), and would not be feasible for quickly needed results. Additionally, bacteria growth is dependent upon nutrient availability, electron donors present, as well as pH and salinity. Determining rate constants from microbial data introduces uncertainties derived from each unknown. Furthermore, different bacteria species may affect the system differently, thus the rate constants derived through experiments may be largely contingent upon the bacteria strains that were used.

Chemical Reducing Agent Techniques

Chemical reducing agents have also been used in order to obtain reducing conditions (Ribet et al., 1995; Niinae et al., 1996; Davranche et al., 2000; Davranche et al., 2000; Zhang et al., 2001; Chi et al., 2002; Davranche et al., 2003; Smolen et al., 2003; Temple, 2003; Chatain et al., 2005). Examples of chemicals that have been used in this capacity include: sodium ascorbate, hydroxylamine, ammonium thiosulfate, ammonium sulfite, sodium borohydride, ascorbic acid, hydroxybenzene, o-dihydroxybenzene, m-dihydroxybenzene, p-dihydroxybenzene, o-trihydroxybenzene, and m-trihydroxybenzene.

Sodium borohydride and sodium ascorbate have been used in order to determine the mobility of arsenic in soils over a range of redox conditions. Both of these reducing agents were shown to enhance the dissolution of arsenic (Chatain et al., 2005). Sodium ascorbate has also been used in order to study the mobilization of heavy metals associated with wastes from metallurgical industries in northern France and heavy metals associated with iron oxyhydroxides (Davranche et al., 2000; Davranche et al., 2003).

Ascorbic acid has been used to reduce goethite, in order to determine the affect that the dissolution would have on organic pollutants. In the case of the organic pollutant 4-cyanonitrobenzene, the dissolution of goethite then promotes the reduction of this compound (Smolen et al., 2003).

Hydroxylamine was used in order to study heavy metals and their association with both iron and manganese oxyhydroxides (Davranche et al., 2000).

Ammonium thiosulfate and ammonium sulfite were used in order to leach copper, cobalt, and nickel from cobalt-rich ferromanganese crusts (Niinae et al., 1996). The phenol-type aromatic compounds (hydroxybenzene, o-dihydroxybenzene, m-dihydroxybenzene, p-dihydroxybenzene, o-trihydroxybenzene, and m-trihydroxybenzene) were used in order to extract heavy metals from Pacific Ocean manganese nodules (Zhang et al., 2001). The goal of leaching minerals from both cobalt-rich ferromanganese crusts and manganese nodules is to obtain the heavy metals for use when terrestrial supplies become depleted.

The advantages of the use of chemical reducing agents are that they: 1) can be completed in a short time frame (several days) and 2) eliminate the uncertainties in using microbial populations. The main disadvantage of chemical reducing agents is that they may interfere with the chemistry of the soil or waste material, which could affect the results.

Electrolytic Techniques

Electrolytic techniques are based on cyclic voltammetry techniques and involve the use of a potentiostat, an electrochemical cell, and a three-probe system. Electrolytic techniques consist of passing an electric current through a suspension. The potentiostat provides the source of electrons for the reactions to occur within the electrochemical cell. The electrochemical cell is a vessel that contains a three-probe system and the waste to be oxidized or reduced. The cell may also contain an entrance/exit for nitrogen gas, a sampling port, Eh and pH probes, and a stir bar.

The three-probe system consists of a working electrode, a reference electrode, and a counter or auxiliary electrode. Three probes are used in order to eliminate the potential drop that would occur in a two-probe system, as well as allowing the current to pass through the cell without affecting the potential. The working electrode is the site of the reactions of interest in the cell, which occur at the electrode surface. The reference electrode is the standard through which the potential of working electrode is controlled, and must consist of a material that does not change potential over time. The auxiliary or counter electrode closes the circuit by accepting the electrons entering the system through the working electrode.

The system is limited by the optimum range of the working electrode, which varies based on the material used. Outside this range, the working electrode degrades and can foul the system. Examples of the potential windows of three types of working electrodes are presented in Figure 10.

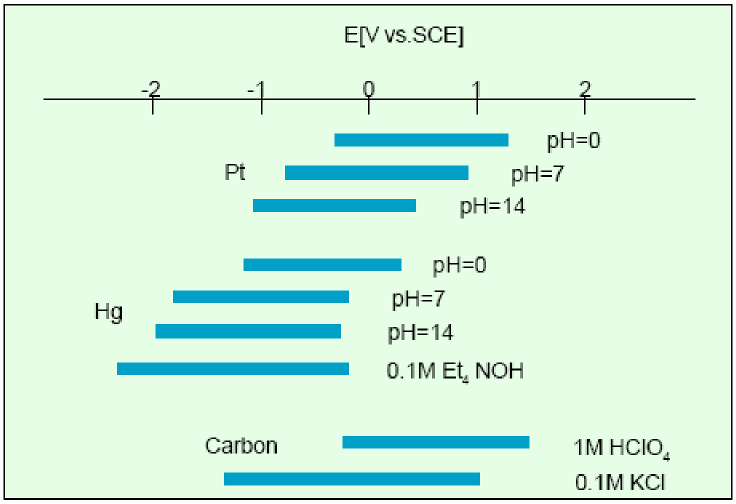


Figure 10. Potential windows of three working electrodes (SCE is +0.241 v. NHE) (http://www.ijcambria.com).

The mechanisms that occur within the electrochemical cell are as follows: 1) mass transfer of solutes from/to the bulk solution to/from the electrode surface, 2) electron transfer at the electrode surface, 3) adsorption/desorption of the solute at the surface, and 4) subsequent reactions that may occur within the cell (Bard et al., 2001). The mechanisms that affect the transfer of solutes from/to the bulk solution to/from the electrode surface include diffusion, migration, and convection.

Electrolytic techniques have been proposed to control the redox state of sediments (Miller et al., 1993). A diagram of the electrochemical cell by Miller, et al. (Miller et al., 1993) is presented in Figure 11. The potentiostat provides a source of electrons, which then react with the chemical species present in the bulk solution. The system used a copper sponge as the working electrode, a platinum wire as the counter electrode, and a silver wire as the reference electrode. The objective of the work was to analyze soil samples to understand the reducing conditions that occur when soils experience anoxic conditions. Iron reduction similar to that which occurs as a result of microbial activity was observed; however, the simulations required 150mV more voltage than is required when using microbes. Kumari, et al. (Kumari et al., 2002) developed a similar electrochemical cell in order to study the leaching of Cu, Ni, and Co and were able to show a correlation between the increase in metal release with a decrease in applied potential.

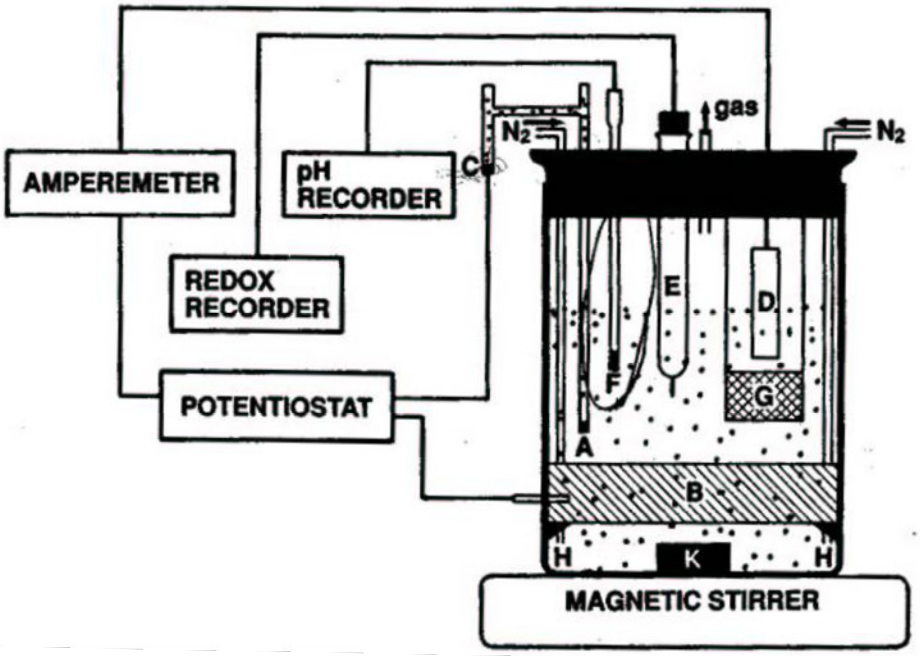


Figure 11. Diagram of apparatus for controlling the electrolysis of soil suspensions, where B is the copper sponge working electrode, G is the salt bridge, D is the platinum counter electrode, and A is the silver reference electrode (Miller et al., 1993).

Electrodialytic techniques have also been developed to change the oxidation state of metals in soils (Hansen et al., 2005; Pedersen et al., 2005; Christensen et al., 2006). This technique involves the use of membranes that compartmentalize the waste from the cathode and the anode. A schematic of the cell is presented in Figure 12 (Rojo et al., 2006). The contaminants within the soil are moved as ions due to the applied current, which is depicted in Figure 13 (Acar et al., 1995). This technique has been used to remove heavy metals such as copper, cadmium, lead, zinc, chromium, mercury, and arsenic from mine tailings, fly ashes, soils, refuse, CCA-treated wood waste, and wastewater sludge (Velizarova et al., 2002; Pedersen, 2003; Jakobsen et al., 2004; Velizarova et al., 2004; Hansen et al., 2005; Pedersen et al., 2005; Christensen et al., 2006; Nystroem et al., 2006; Rojo et al., 2006).

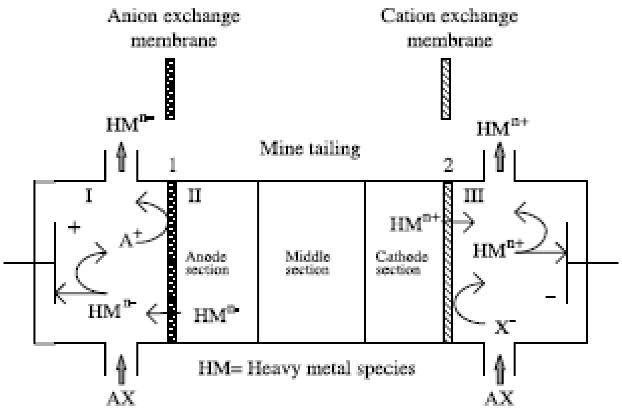


Figure 12. Representation of the electrodialytic remediation technique (Rojo et al., 2006).

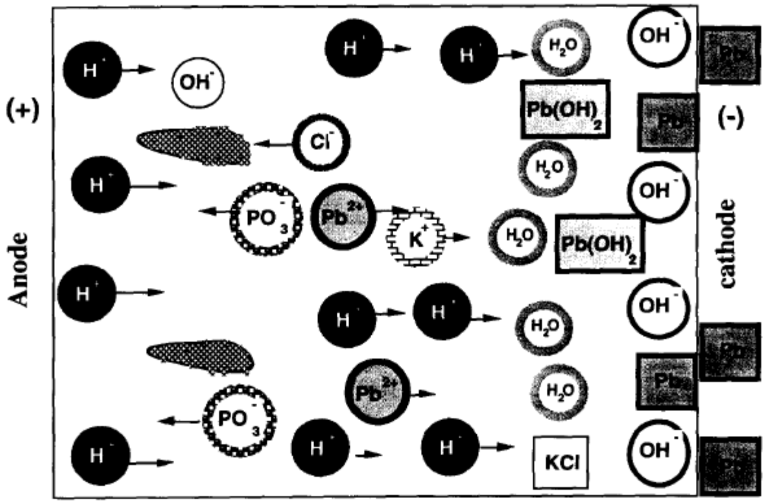


Figure 13. Movement of ions as a results of current passing through the system (Acar et al., 1995).

Research Objectives

The issue of the effect of oxidation/reduction conditions on the mobility of inorganic contaminants still remains an underdeveloped area of research. There is a need for laboratory tools that would allow the assessment of the mobility of contaminants using experimentally induced and controlled reducing or oxidizing conditions. Developing such a technique will contribute to a better understanding of the fate and transport of contaminants under different leaching scenarios. Although work has been done using biological technique and chemical reducing agents, these methods have limitations. In contrast, the use of electrolytic techniques to study the mobility of species under reducing and oxidizing conditions presents the following advantages: 1) a relatively shorter amount of time (oxidation/reduction can be seen within hours) in comparison with the biological methods, 2) no dependence upon microbial activity, 3) and no artifacts due to chemical reducing agents. The objectives of this research were to: 1) develop an apparatus based on electrolytic techniques and 2) use the apparatus to determine the mobility of redox-sensitive species in soils and waste materials over a range of pH and Eh values.

CHAPTER III

MATERIALS AND METHODS

Experimental Design

In order to meet the research objectives, two different types of studies were performed: 1) preliminary studies of sampled-current voltammetry experiments that consisted of cyclic potential sweeps and 2) electrolytic oxidation/reduction studies of three types of materials under a range of applied potentials.

In the first set of studies, sampled-current voltammetry experiments were run in order to determine the effect of different parameters on the electrolytic system. Two types of working electrodes, copper and carbon, were evaluated. The salt in the salt bridge was also alternated between sodium chloride and potassium nitrate. Finally, two forms of iron(III) (a soluble and insoluble form) were used as a model system.

In the second set of studies, the electrolytic technique was used to evaluate the oxidation or reduction of three different suspensions: 1) iron(III) nitrate, 2) arsenic contaminated soil, and 3) furnace slag. Different applied potentials were examined for a total of six hours. The effects of time and varying applied potentials on changes in suspension pH, Eh, and constituent concentration were investigated. The constituents of interest were 1) iron (iron(III) nitrate solution), 2) iron, arsenic, and copper (arsenic contaminated soil), and 3) iron, arsenic, copper, strontium, and barium (furnace slag).

Electrolytic Apparatus

A Potentiostat/Galvanostat Model 273 (EG&G Princeton Applied Research; Oak Ridge, TN) was used in conjunction with a three-probe system to apply negative and positive potentials. The three-probe system is composed of: 1) a working electrode, 2) a reference electrode, and 3) an auxiliary or counter electrode. A schematic and photo of the cell and three-probe system are presented in Figure 14 and Figure 15, respectively.

In the preliminary studies, different working electrodes were used including copper sponges (Product No. 425, LOLA Products; Hackensack, NJ), copper pipes (Soft Copper 1/4L by 2 Handi Length, Home Depot; Nashville, TN), and a carbon rod (zinc-chloride battery). The copper sponge was immediately discarded as a usable working electrode due to the fact that the copper plating entered the solution as soon as any potential was applied. In the second set of studies, the carbon electrode was chosen as the working electrode. This electrode was chosen because it was inert and was capable of being used over a broad range of both positive and negative potentials (-1800 to +2000mV) without degradation.

The reference electrode that was used was a 0.5 mm 99.9% silver wire (World Precision Instruments, Inc.; Sarasota, FL). This electrode was placed physically close to the working electrode to limit the interference within the cell.

The counter or auxiliary electrode was a 32 gauge platinum wire (Fisherbrand, Fisher Scientific Company; Pittsburgh, PA) and was physically separated from the suspension via a salt bridge. The salt bridge consisted of a polypropylene tube (Fisherbrand, Fisher Scientific Company; Pittsburgh, PA) filled with a 1M potassium nitrate (Fisherbrand, Fisher Scientific Company; Pittsburgh, PA) agar (Acros Organics;

Geel, Belgium) solution. Sodium chloride (Fisherbrand, Fisher Scientific Company; Pittsburgh, PA) was also used as the salt for the salt bridge; however, testing showed little difference between using the sodium chloride and the potassium nitrate. The platinum wire was then inserted into the agar in order to complete the circuit.

The three-probe system was contained within a 250mL polypropylene container with locations drilled into the container's lid for each of the three probes. The probes were surrounded by Parafilm® (Pechiney Plastic Packaging; Chicago, IL) in order to prevent the entrance of oxygen into the closed system. A pH and Eh probe were also inserted directly into the cell in order to obtain direct measurements. The cell contained two additional holes for the entrance and exit of nitrogen gas and a sampling port. The cell was continuously kept under a blanket of nitrogen by inserting a tube into the headspace above the suspension. The exit tube served as the exit for the nitrogen gas, as well as a sampling port.

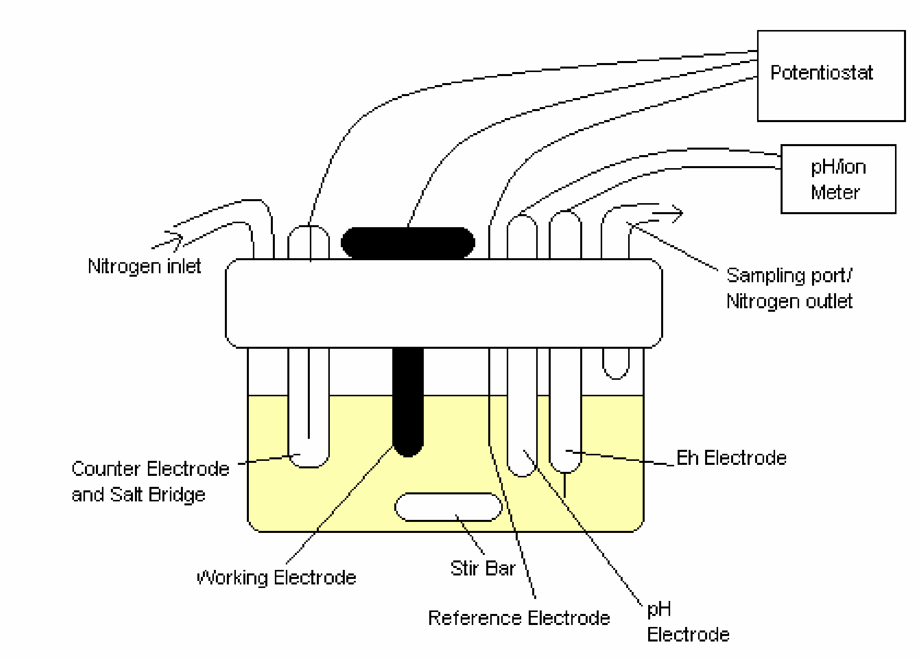


Figure 14. Schematic of the electrolytic cell and three-probe system.

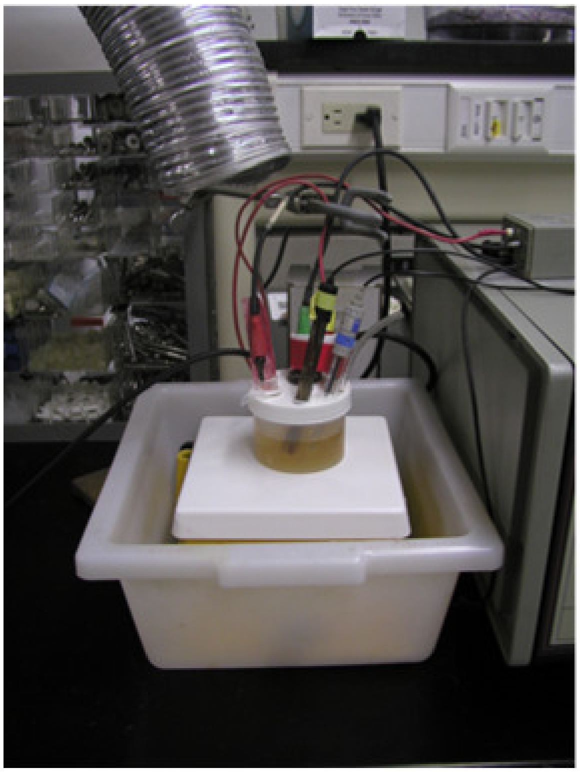


Figure 15. The electrolytic cell and three probe system.

Materials

Three different types of suspensions were used for this study: 1) iron(III) nitrate, 2) arsenic contaminated soil, and 3) furnace slag. The iron(III) nitrate solution was used as a test system. The arsenic contaminated soil was used as a representative of a natural oxidized system. The furnace slag was used as a representative of a reduced system.

Iron(III) Nitrate Solution

A solution of 0.006M iron(III) nitrate nonahydrate (Aldrich Chemical Company, Inc.; Milwaukee, WI) was used in the preliminary experiments, while a concentration of 0.01M was used in the second set of studies. Iron(III) nitrate nonahydrate is a lavender, crystalline solid that is completely soluble in water. Iron(III), or Fe^{+3}, is the oxidized oxidation state of iron. The initial pH of the iron(III) nitrate solution was around 2.5, and the Eh of the solution was approximately 830mV (v. NHE).

Soil Suspension

The arsenic contaminated soil was obtained from a gold mining site in France. This soil has been previously used in experiments conducted by Chatain (Chatain et al., 2003; Chatain, 2004; Chatain et al., 2005; Chatain et al., 2005). The natural pH of the soil was around 6.6, and the Eh of the soil was approximately 320mV. The total content of major constituents and trace metals are presented in Table 2.

Table 1. Total content of major constituents and trace metals in the arsenic contaminated soil as determined by acid digestion (Chatain et al., 2005).

Major Elements		Total Content (%)
Silicon	Si	20.3
Iron	Fe	8.9
Aluminum	Al	4.3
Calcium	Ca	3.7
Sulfer	S	2.1
Potassium	K	1.9
Magnesium	Mg	0.6
Sodium	Na	0.1
Trace Elements		Total Content (mg/kg)
senic	As	27700
Copper	Cu	1700
Lead	Pb	800
Manganese	Mn	400
Zinc	Zn	400

Furnace Slag Suspension

The blast furnace slag was obtained from the Pacific National Northwest Laboratory (PNNL). The natural pH of the material was around 12, and the natural Eh was around 120mV. The total content of major constituents and trace metals are presented in Table 3.

Table 2. Total content of major constituents and trace metals in the blast furnace slag as determined by XRF analysis (Garrabrants, 2006).

Major Elements		Total Content (ppm)
Calcium	Ca	186160
Iron	Fe	2860
Potassium	K	2666
Titanium	Ti	1956
Manganese	Mn	1680
Trace Elements		**Total Content (ppm)**
Strontium	Sr	323
Barium	Ba	252
Cobalt	Co	119
Nickel	Ni	100
Zirconium	Zr	90
Copper	Cu	57
Arsenic	As	41
Rubidium	Rb	16.9
Thorium	Th	12.2
Uranium	U	8.4
Molybdenum	Mo	8.2

Electrolyte solution

0.5M potassium nitrate and 0.5M sodium chloride were used as the electrolyte solution. Prior to use, these solutions were degassed by sparging water-saturated nitrogen gas for a minimum of one hour. The electrolyte solution was added in order to enhance conductivity and therefore minimize the resistance between the working and the reference electrodes (Miller et al., 1993). This solution was chosen on the basis of solubility and inertness.

Preliminary Studies

Objective

The objectives of the preliminary studies were to determine the effects of different salt bridges, working electrodes, and iron sources on the Eh, pH, and Faradic current of the electrolytic cell. For this purpose, sampled-current voltammetry experiments consisting of cyclic potential sweeps from 0 to -2000mV (forward sweep) and then from -2000 to 0mV (reverse sweep) were performed.

Procedure

The applied potential was decreased every one minute by -100mV until -2000mV was reached (forward sweep). At this point, the potential was increased every one minute by +100mV until the applied potential was cycled back to the beginning applied potential of 0mV (reverse sweep). For each increment, after one minute at the applied potential of concern, the potentiostat was momentarily stopped, and the Eh and pH were measured in situ (in the electrolytic cell).

Two chemicals were used as a source of iron(III): 1) 0.006M iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) and 2) 0.01M ferric oxide (Fe_2O_3). Each iron source was added to 75mL of 0.5M sodium chloride in Milli-Q Plus deionized water.

Two types of working electrodes were examined: 1) a copper pipe and 2) a carbon rod. The reference electrode was 0.5mm diameter 99.9% silver wire. The auxiliary electrode was a 32 gauge platinum wire separated from the bulk solution through a salt bridge.

Two types of salt bridges were made using 1) sodium chloride and 2) potassium nitrate. The salt bridges were formed using 75mL of Milli-Q Plus deionized water that was heated to boiling. 1.5g of Agar was added, followed by 1M of the salt once the solution was removed from the heat.

0.5M sodium chloride was used as the electrolyte solution for each experiment in the preliminary set of studies.

A total of eight experiments were completed, with 2 replicates for each experiment. Table 4 summarizes the test conditions.

Table 3. Sampled-current voltammetry experiments comparing iron sources, working electrodes, and the salt component of the salt bridge.

Experiment #	**Iron Source**	**Working Electrode Type**	**Salt used in Salt Bridge**
1	$Fe(NO_3)_3 \cdot 9H_2O$	Carbon rod	NaCl
2	$Fe(NO_3)_3 \cdot 9H_2O$	Carbon rod	$K(NO_3)$
3	$Fe(NO_3)_3 \cdot 9H_2O$	Copper pipe	NaCl
4	$Fe(NO_3)_3 \cdot 9H_2O$	Copper pipe	$K(NO_3)$
5	Fe_2O_3	Carbon rod	NaCl
6	Fe_2O_3	Carbon rod	$K(NO_3)$
7	Fe_2O_3	Copper pipe	NaCl
8	Fe_2O_3	Copper pipe	$K(NO_3)$

Oxidation/Reduction Studies using an Electrolytic Technique

Objective

The objectives of these studies were to determine 1) the effect of time for an applied potential on changes in suspension pH, Eh, and constituent mobility and 2) the effect of varying applied potential on changes in suspension pH, Eh, and constituent mobility.

Procedure

A 0.1M iron(III) nitrate solution in a 0.5M potassium nitrate solution was used as a test system. For this solution, the applied potentials of 0mV, -200 mV, -1200mV, -1400mV, -1600mV, and -1800mV were evaluated. The solutions were continuously agitated throughout the experiment.

For the arsenic contaminated soil, 0.5M potassium nitrate was used as the electrolyte solution. A liquid-to-solid ratio (LS ratio) of 10mL/g was used. The applied potentials of -1200mV, -1400mV, and -1600mV were examined. The suspensions were continuously agitated throughout the experiment.

For the furnace slag, 0.5M potassium nitrate and 0.05M EDTA were used as the electrolyte solutions. The applied potentials of +1600mV and +2000mV were examined for each system. Again, a LS ratio of 10mL/g was used, and the suspensions were agitated throughout the experiment.

Each applied potential examined was maintained for a total of six hours, with the exception of 0mV, which was applied for a total of 1.5 hours. Prior to applying a potential, the solution was placed under a blanket of nitrogen gas for a minimum of 30 minutes. The Eh and pH were recorded in situ, prior to and after sampling. A 10mL sample was extracted for measurement of pH, Eh, and preservation with nitric acid in the nitrogen-filled glove bag. After sampling with no applied potential, a potential was applied. Sampling occurred every two hours for a total of six hours. The current was also monitored and recorded after initially applying the potential and every two hours thereafter.

The sampling was done with a needleless syringe and was then transported immediately into the nitrogen-filled glove bag. The sample was then filtered using 0.45μm pore size syringe filters. The filtrate was used to record the bulk solution Eh and pH. Approximately half of the filtrate was acidified using 2% by volume Nitric acid in order to be preserved for analysis using ICP-MS. The second half of the filtrate was used for a qualitative measurement of the iron(II) concentration (Code 3347 Iron Ferric/Ferrous, LaMotte; Chestertown, MD). The test kit provided only ranges of iron(II) concentrations.

Testing Condition Precautions

For this set of electrolytic experiments, oxygen in the system was limited throughout the experiment by the use of nitrogen gas. First, the stock solutions of potassium nitrate were degassed by bubbling nitrogen for over an hour. Second, a blanket of nitrogen gas was circulated over the surface of the suspension within the electrochemical cell for 30 minutes prior to the start of the experiment. This blanket was continued throughout the entirety of the experiment in order to prevent possible reoxidation of constituents due to oxygen. Third, the sampling was completed using a small tube inserted into the cell, again limiting the contact with oxygen. Finally, the syringe was immediately transported into a glove bag, where the external Eh and pH measurements, as well as solution acidification for future analysis using ICP-MS were completed under nitrogen. A picture of the glove bag set-up is shown in Figure 16. The glove bag filled with nitrogen has previously been shown to provide a more accurate measurement of Eh (Temple, 2003; Chatain et al., 2005).

.

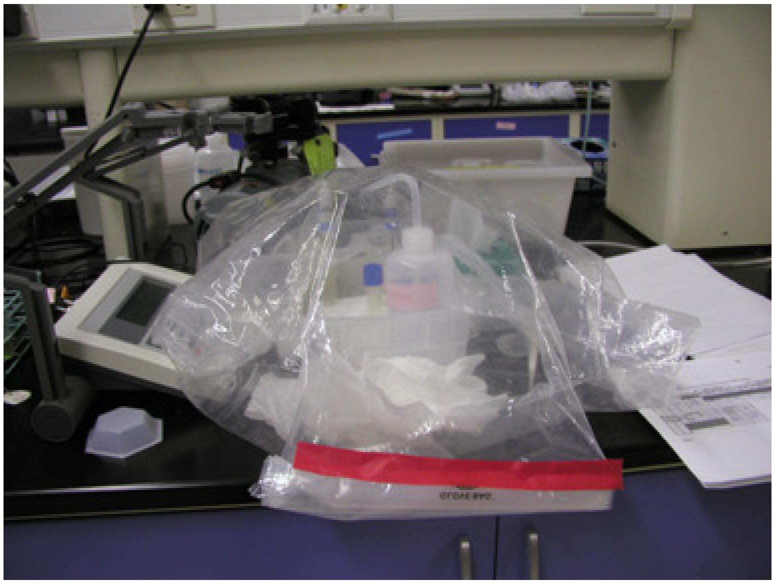


Figure 16. Glove bag filled with nitrogen for external pH and Eh readings for the oxidation/reduction experiments using an electrolytic technique.

Analytical Methods

Eh and pH Measurements

The Eh and pH measurements were made using a Corning pH/ion 450 meter (VWR International; West Chester, PA). An Accumet platinum Ag/AgCl combination electrode was used for the Eh measurements (Fisher Scientific; Pittsburgh, PA). An Accumet combination electrode with Ag/AgCl reference was used for the pH measurements. The Eh electrode sensitivity was checked against two redox solutions of 470 and 200-275mV (Hanna Instruments; Woonsocket, RI). The pH electrode was calibrated against three buffer solutions (4.0, 7.0, and 10.0).

Aqueous Concentration Measurements

The aqueous concentrations of Fe, As, Cu, Sr, and Ba were measured using a PerkinElmer inductively coupled plasma mass spectrometer (ICP-MS) ELAN DRC II (PerkinElmer Instruments; Shelton, CT). Quality assurance was determined through duplicate sample analysis, spiked sample analysis, a 6 point calibration curve, and internal standard during analysis. The detection limits (method detection limit (MDL) and minimum level of quantification (ML)) of each element analyze are presented in Table 4.

Table 4. Detection limits for ICP-MS analysis for arsenic, barium, copper, iron, and strontium.

Element	Symbol	Isotope	STD	MDL (µg/L)	ML (µg/L)
Arsenic (oxide)	AsO	91	0.0261	0.660	3
Barium	Ba	138	0.0081	0.205	1
Copper	Cu	63	0.0192	0.486	2
Iron	Fe	57	0.0489	1.237	5
Strontium	Sr	88	0.0093	0.235	1

Qualitative Measurement of Iron(II) in Solution

The LaMotte iron ferrous/ferric test kit (Code 3347) was used in order to qualitatively assess the amount of iron(II) in solution (LaMotte; Chestertown, MD). The test color standards correspond to iron(II) concentrations of 0.5, 1.0, 2.0, 3.0, 4.0, 6.0, 8.0, and 10.0mg/L. The colors that were obtained using the qualitative measurement of iron(II) for the iron(III) nitrate and arsenic contaminated soil were different hues than were given as test color standards. In these instances, the color intensities of the samples were compared to the intensity of the color standard (as instructed by LaMotte technical assistance).

CHAPTER IV

RESULTS AND DISCUSSION

Preliminary Studies

The objectives of the preliminary studies were to determine the effect of the: 1) source of iron(III), 2) type of working electrode, and 3) type of salt bridge on sampled-current voltammetry experiments.

Effect of the Source of Iron(III)

Iron nitrate and iron oxide were both used in the preliminary studies as iron sources. Iron nitrate is completely soluble, whereas iron oxide is insoluble in water. Results obtained using iron nitrate were found to be consistently more reproducible than those using iron oxide. This was most likely related to the fact that all of the iron nitrate entered into solution. This reproducibility was shown regardless of the type of working electrode or salt bridge used. These findings led to the selection of iron nitrate as the test solution for the second set of experiments (see section entitled “Electrolytic Oxidation/Reduction Studies”, p. 48).

Precipitation of iron was obtained for an applied potential of -1800 to -2000mV. This precipitation event was coupled with a sharp increase of pH from an initial pH of around 2.5 to a final pH of around 12. After the solution reached the pH of 12, the pH stabilized and additional decrease in the applied potential did not further change the pH.

During the precipitation event, the measured Eh decreased from 825mV to about 100mV. When the applied potential was cycled back from -2000 to 0mV, the bulk solution did not return to the initial bulk Eh and pH. The Eh and pH results are shown in Figure 17.

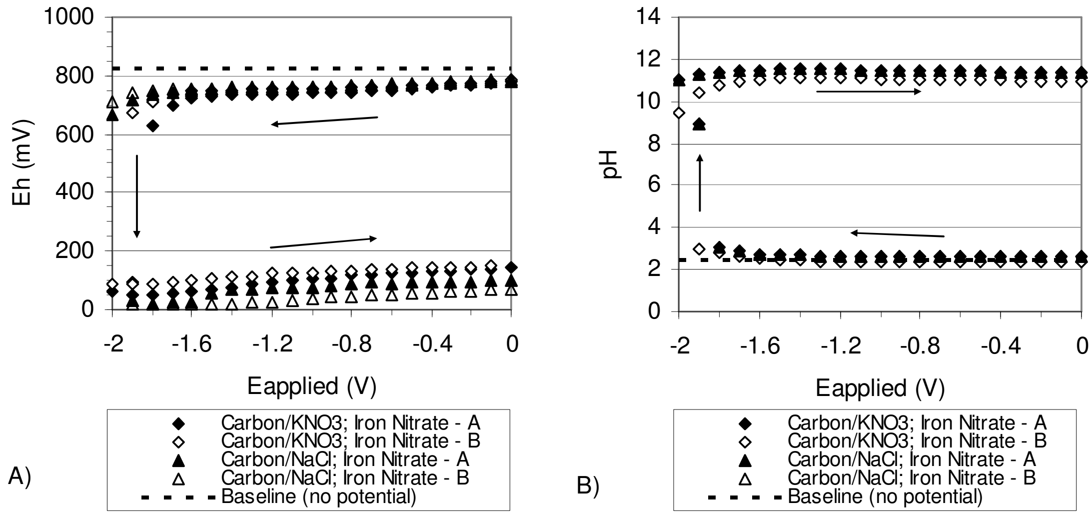


Figure 17. Shift in the A) measured Eh and B) pH as a function of applied potential for the 0.006M iron(III) nitrate solution.

Effect of the Type of Working Electrode

Two types of working electrodes were investigated: a copper pipe and a carbon rod. When iron nitrate was used as the iron source, the results were reproducible and similar indicating that the two types of working electrodes behaved similarly under like conditions. Results comparing the Eh, pH, and current of the copper pipe and the carbon rod are presented in Figure 18.

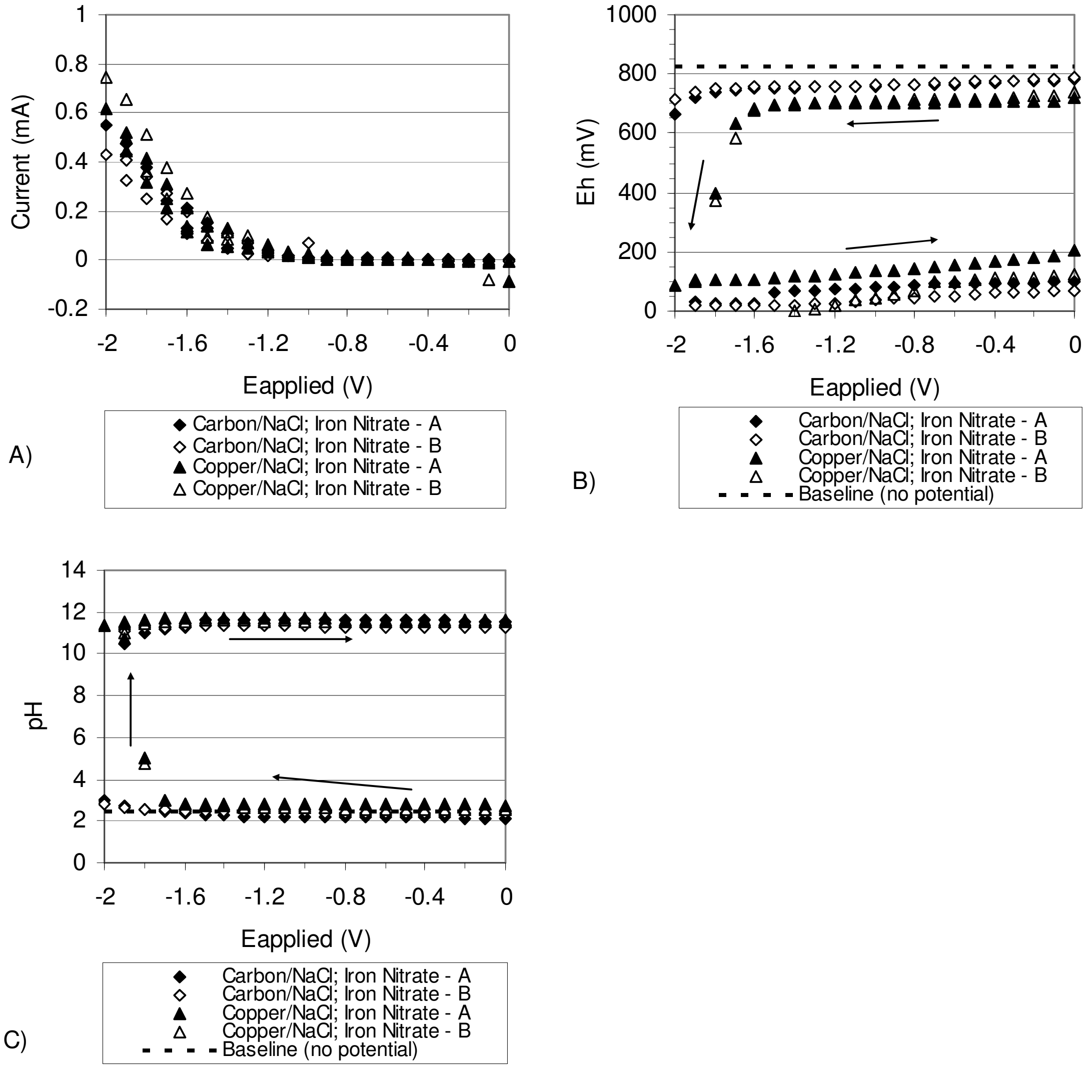


Figure 18. Comparison of the use of a copper pipe and a carbon rod as the working electrode for a 0.006M iron nitrate solution. A) Current as a function of applied potential. B) Measured Eh (v. NHE) as a function of applied potential. C) pH as a function of applied potential.

Effect of the Type of Salt Bridge

Potassium nitrate and sodium chloride were used for the salt bridge. As shown in Figure 17, the two different types of salt bridges performed similarly for a solution of 0.006M iron nitrate in 0.5M sodium chloride (electrolyte solution). Ultimately, a potassium nitrate salt bridge and a 0.5M potassium nitrate electrolyte solution were used. This was in order to limit the chemical constituents that would come into contact with the material that was being studied.

The current in these experiments did not follow the typical shape generally observed for cyclic voltammograms (CVs). During the forward sweep the oxidized form is reduced, which is generally characterized by the presence of a peak. During the reverse sweep the reduced form is oxidized, which is generally characterized by the presence of a reverse peak (Gosser, 1993). None of these peaks were observed. This was most likely due to the fact that the peaks were masked by the background current of the reduction of oxygen and water on the electrode surface (Grygar et al., 2002).

Conclusions

For the preliminary studies, iron(III) nitrate was chosen to be used in further studies as a test solution due to its solubility. The carbon rod did not appear to adversely affect the system and was chosen as the working electrode for subsequent studies. Finally, little difference was seen between the use of potassium nitrate and sodium chloride in the salt bridges. In order to eliminate extraneous ions in solution, potassium nitrate was chosen to be used in the salt bridge and the electrolyte solution in subsequent studies.

Electrolytic Oxidation/Reduction Studies

Effect of Time during the Electrolysis

The effect of time on electrolytic reduction was analyzed for a test solution of iron(III) nitrate and an arsenic contaminated soil. The effect of time of on electrolytic oxidation was analyzed for a furnace slag. Faradic current, Eh, and pH were measured and evaluated for each system as a function of time. The aqueous concentrations of 1) Fe (iron(III) nitrate solution), 2) Fe, As, and Cu (arsenic contaminated soil), and 3) Fe, As, Cu, Ba, and Sr (furnace slag) were also measured as a function of time.

For the results presented in the following sections, the baseline current for the current graphs corresponded to the current of the electrolyte solution (0.5M potassium nitrate or 0.05M EDTA) at the applied potential being observed. The baseline for both the Eh and pH measurements corresponded to the bulk Eh and pH measurements obtained in the suspensions (material in electrolyte solution) when no potential was applied.

Iron Nitrate Solutions

For the iron(III) nitrate solutions, an applied potential of 0, -200, -1200, -1400, -1600, and -1800mV were examined. For the 0 and -1800mV, the potential was applied for 1.5 hours, whereas the potential was applied for a duration of 6 hours for the remaining potentials.

For each applied potential examined, a common format is used for presenting the results. Two sets of figures are used. In the first set of figures, figures A, B, C, and D show the current, bulk solution Eh, pH and iron concentration as a function of time, respectively. In the second set of figures, photographs depicting the qualitative change of iron(II) in solution are provided for the applied potentials of 0, -1200, -1400, -1600, and -1800mV.

Applied potential of 0mV (Figures 19 and 20)

At the applied potential of 0mV, no change in color of the bulk solution was noted. No significant change was observed in the current, pH, and the iron concentration for the 1.5 hours examined. Good replication was obtained for these results. The current remained around 1mV above the baseline for the entire experiment. A small decreasing trend in the Eh of around 50mV was observed over the 1.5 hour period. No significant change in the pH was, however, observed (pH remained at 2.5). These results are shown in Figure 19.

The amount of iron(II) increased in solution from less than 0.5mg/L to 3-4mg/L after 1.5 hours at an applied potential of 0mV (Figure 20). This suggested that the iron in solution was reduced from the iron(III) form to an iron(II) form; however, no significant change in the amount of total iron in solution was observed (concentration of iron in solution remained about 480mg/L).

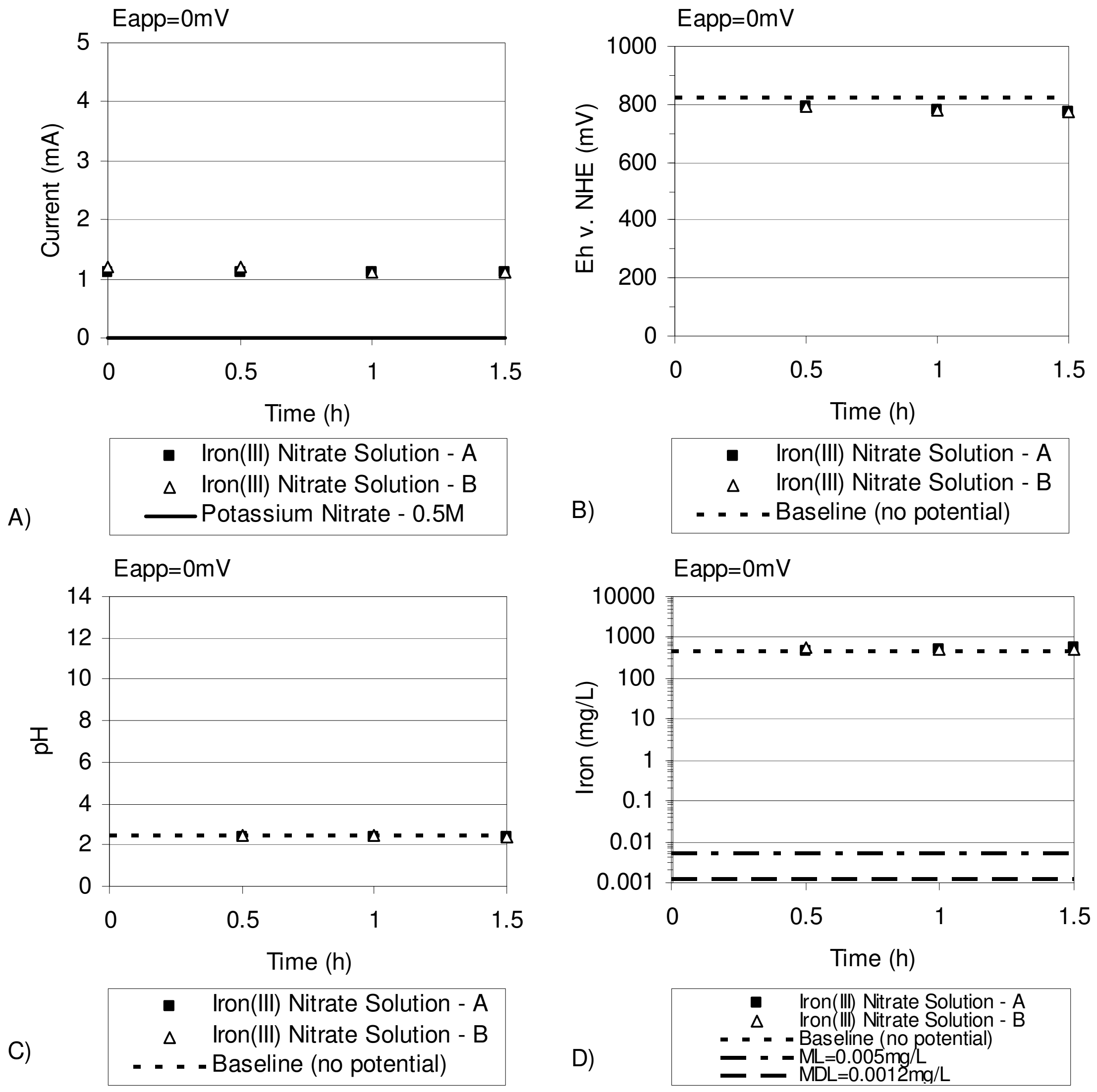


Figure 19. Electrolysis of a 0.01M iron(III) nitrate solution at an applied potential of 0mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time. D) Aqueous phase concentration of iron as a function of time.

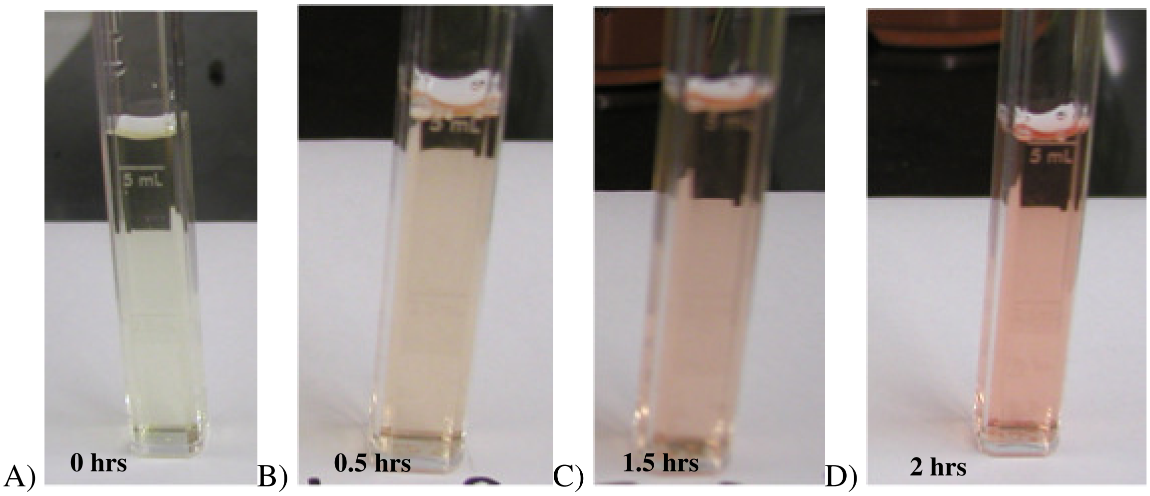


Figure 20. Qualitative measurement of iron(II) in solution at an applied potential of 0mV after A) 0 hours, B) 0.5 hours, C) 1 hour, and D) 1.5 hours of electrolysis. A darker color correlates to a greater amount of iron(II) in solution.

Applied Potential of -200mV (Figure 21)

At the applied potential of -200mV, no color change in the bulk solution was observed. Good replication was obtained. The current decreased as a function of time from 3.7 to 1.6mA, which was above the baseline current (current of the electrolytic solution alone) of 0.1mA. The measured Eh of the bulk solution also showed a decrease of 100mV from its initial value of 825mV during the experiment. The bulk pH remained around 2.5, and the iron concentration in solution remained stable at 480mg/L. These results are shown in Figure 21. A qualitative measurement of the amount of iron(II) in solution was not performed for this set of experiments.

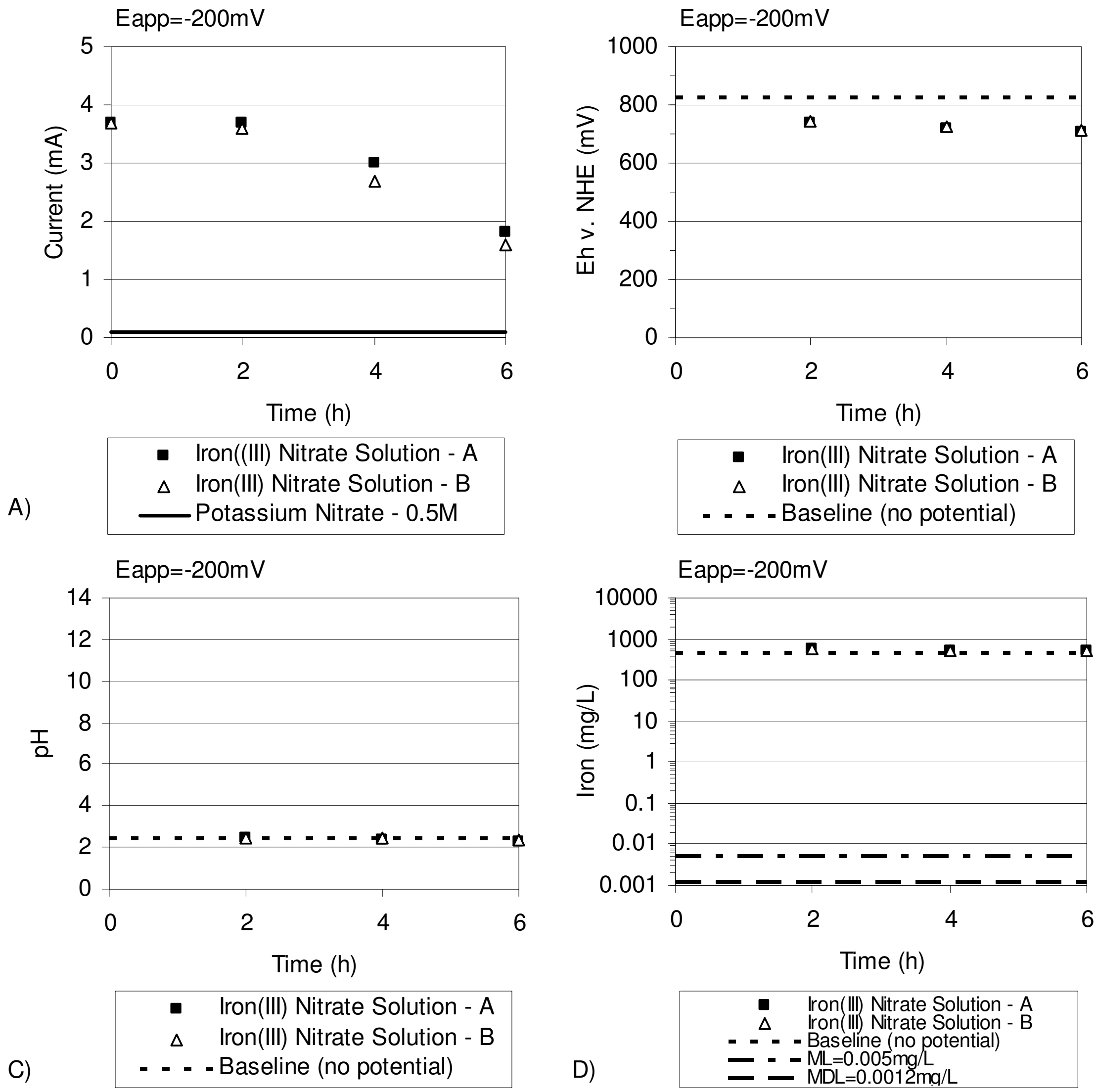


Figure 21. Electrolysis of a 0.01M iron(III) nitrate solution at an applied potential of -200mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time. D) Aqueous phase concentration of iron as a function of time.

Applied Potential of -1200mV (Figures 22-24)

At the applied potential of -1200mV, the current decreased as a function of time from around 15mA to 5mA after six hours, which was higher than the baseline current of 2mA. Overall, a good replication was observed for the bulk solution Eh, pH, and iron concentration. The measured Eh decreased by 50mV over time, which was less than the decrease of 100mV observed in the experiment at an applied potential of -200mV. The pH and the total iron concentration in solution did not significantly change over the course of the experiment. The bulk pH remained around 2.5, and the iron concentration in solution remained stable at 480mg/L. These results are shown in Figure 22. Over the course of the experiment, the solution changed from a pale yellow to a golden orange, as shown in Figure 23.

The amount of iron(II) increased in solution from less than 0.5mg/L to 5-6mg/L after 4 hours at the applied potential of -1200mV, and was followed by a subsequent decrease to approximately 3-4mg/L for times greater than 4 hours (Figure 24). This suggested that the iron(II) level peaked in solution after 4 hours, before decreasing again. This is different than what was observed at the applied potential of -200mV and 0mV, where the iron(II) in solution appeared to increase throughout the experiment. The iron in solution appeared to have been reduced from the iron(III) form to an iron(II) form; however, no precipitate was formed and no significant change in the amount of total iron present in solution was observed (concentration of iron in solution remained around 480mg/L).

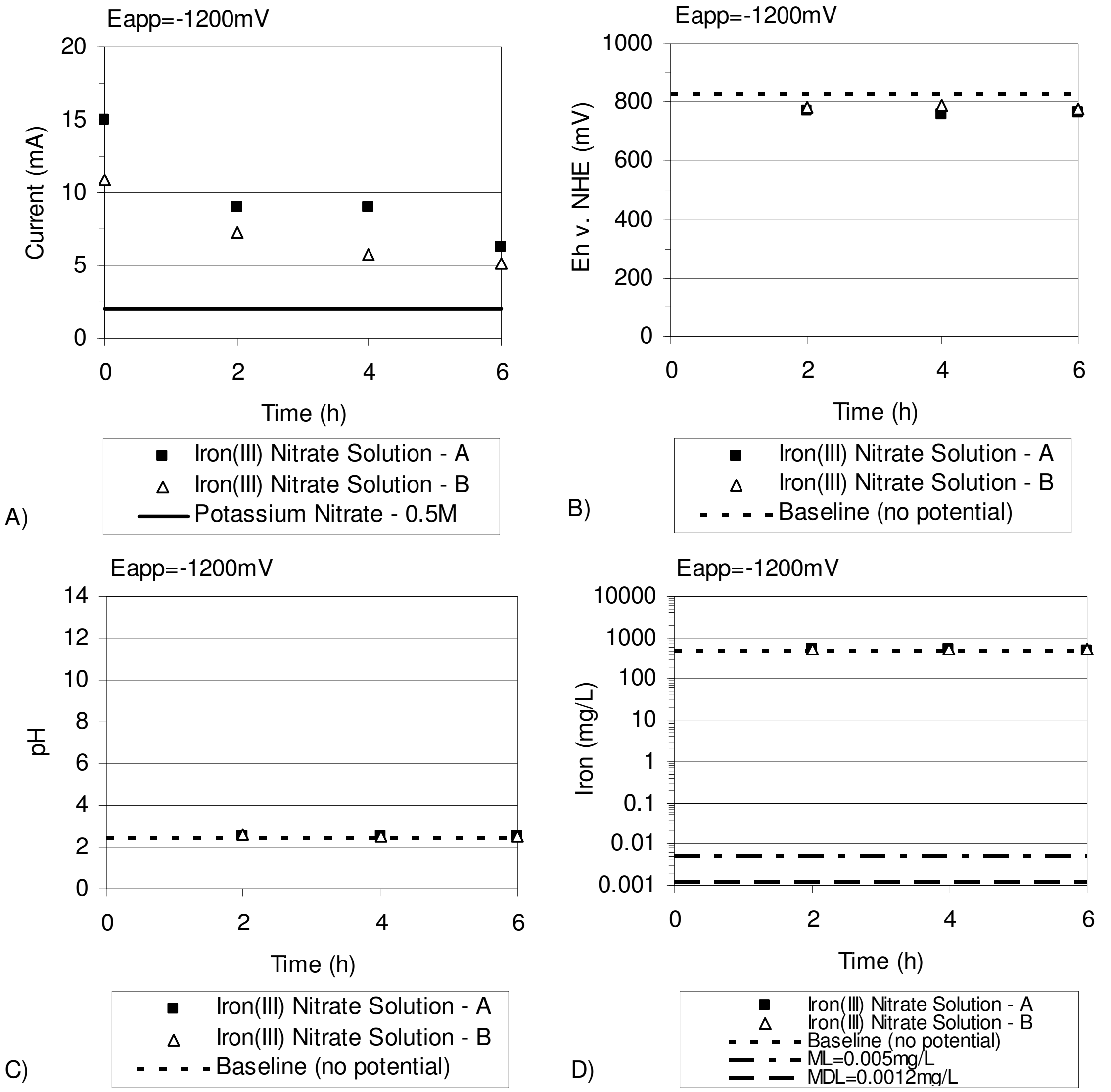


Figure 22. Electrolysis of a 0.01M iron(III) nitrate solution at an applied potential of -1200mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time. D) Aqueous phase concentration of iron as a function of time.

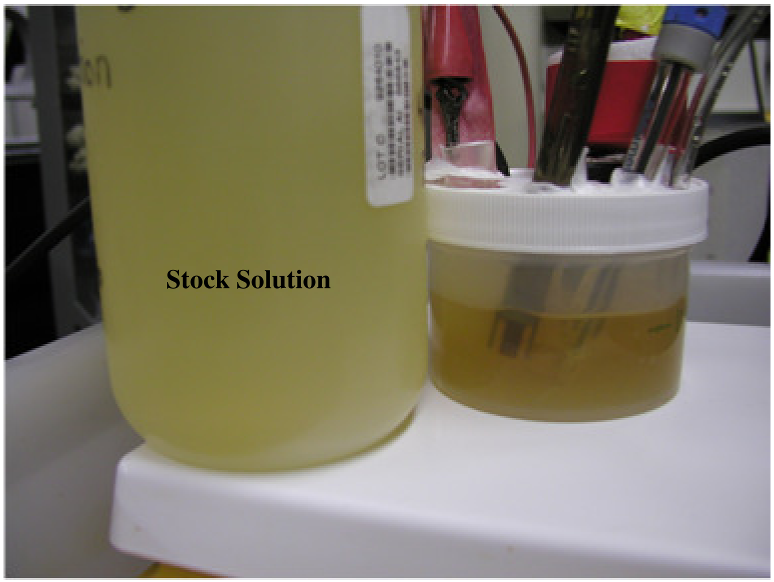


Figure 23. Color change of electrolytic solution after applying a potential of -1200mV in comparison to the 0.01M iron(III) nitrate stock solution.

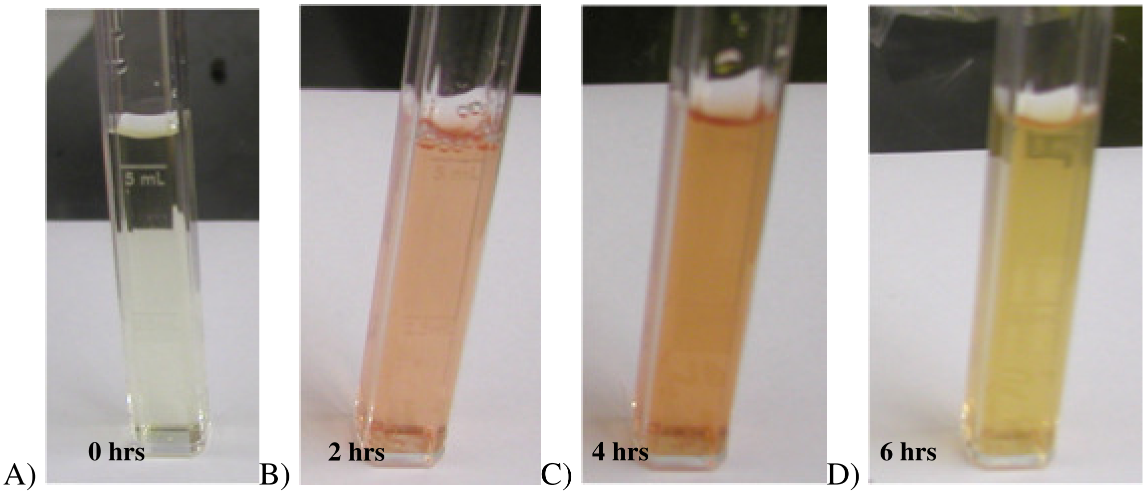


Figure 24. Qualitative measurement of iron(II) in solution at an applied potential of -1200mV after A) 0 hours, B) 2 hours, C) 4 hours, and D) 6 hours of electrolysis. A darker color correlates to a greater amount of iron(II) in solution.

Applied Potential of -1400mV (Figures 25 and 26)

At the applied potential of -1400mV, good replication of the data was obtained overall. The current decreased as a function of time from around 18mA to the baseline current of 4.3mA after six hours. The measured Eh decreased by a total of 40mV over 6 hours, which was similar to the bulk change in Eh observed at the applied potential of 0 and -1200mV. The pH and the total iron concentration in solution remained constant throughout the course of the experiment (around 2.5 and 480mg/L, respectively). These results are shown in Figure 25.

The amount of iron(II) increased in solution from less than 0.5mg/L to 6mg/L after 4 hours of electrolysis at the applied potential of -1400mV, and decreased thereafter to approximately 3-4mg/L for longer electrolysis times (Figure 26). This suggested that the iron(II) level peaked in solution after 4 hours, before decreasing again. These results were similar to the qualitative results obtained at an applied potential of -1200mV. The iron in solution appeared to have been reduced from the iron(III) form to an iron(II) form; however, no significant change in the amount of total iron in solution was observed (concentration of iron in solution remained about 480mg/L).

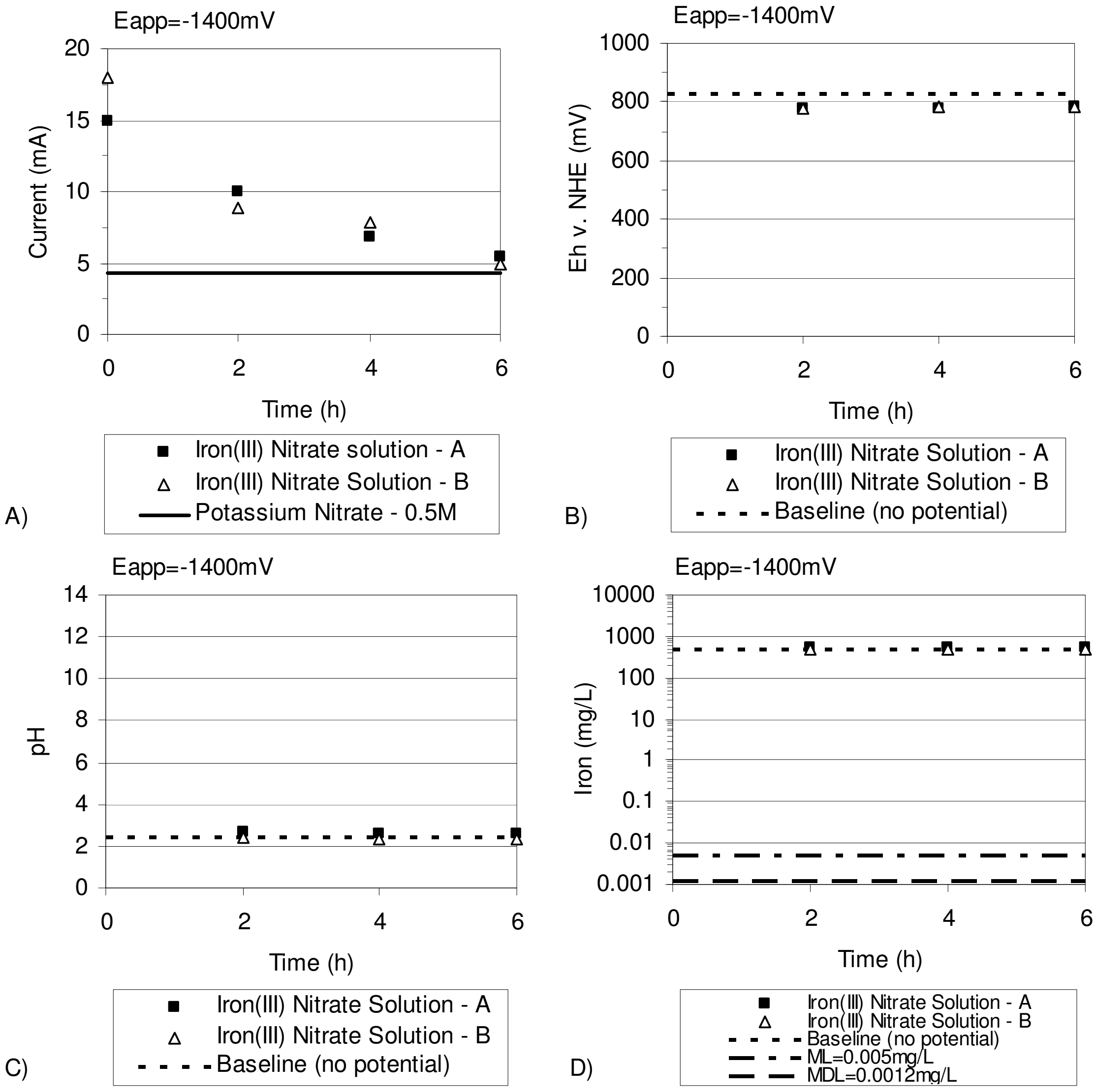


Figure 25. Electrolysis of a 0.01M iron(III) nitrate solution at an applied potential of -1400mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time. D) Aqueous phase concentration of iron as a function of time.

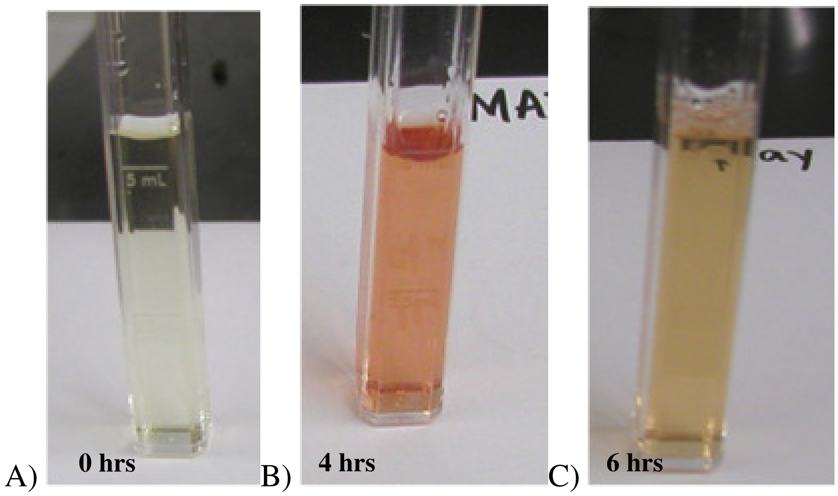


Figure 26. Qualitative measurement of iron(II) in solution at an applied potential of -1400mV after A) 0 hours, B) 4 hours, and C) 6 hours of electrolysis. A darker color correlates to a greater amount of iron(II) in solution.

Applied Potential of -1600mV (Figures 27 and 28)

At the applied potential of -1600mV, the current for one replicate remained stable around 50-60mA, whereas the second replicate increased to 100mA before decreasing to 55mA after 6 hours. The measured Eh decreased from an initial Eh of 825mV to 120mV for both replicates. Although after 6 hours of electrolysis the final Eh values of both replicates were similar (around 120mV), the rate at which the Eh was decreased differed between the two replicates. The pH increased from an initial value of 2.5 to 10. Again, the rate at which the pH decreased differed between the two replicates. The drop in Eh and pH occurred simultaneously with the formation of a gold-brown precipitate. The formation of the precipitate may be responsible for the different rates of Eh and pH decrease. The results of the amount of aqueous iron in solution had poor reproducibility, but both showed a significant decrease in iron from 480mg/L to below 10mg/L, which confirmed that iron precipitated out. These results are shown in Figure 27.

The amount of iron(II) increased in solution from less than 0.5ppm to 1-2ppm after 2 hours of applied potential and decreased thereafter in conjunction with the formation of a precipitate (qualitative test became colorless) (Figure 28).

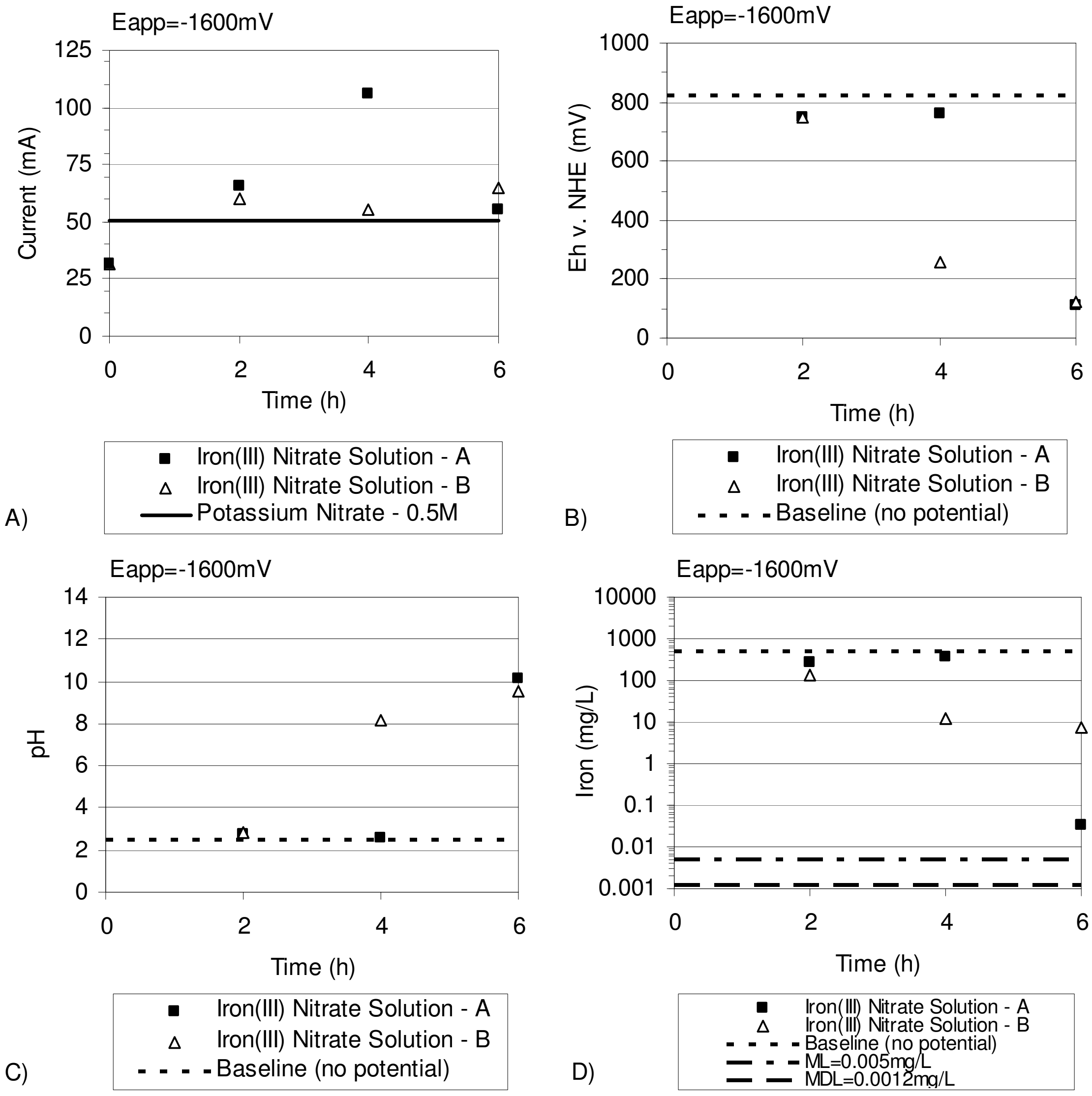


Figure 27. Electrolysis of a 0.01M iron(III) nitrate solution at an applied potential of -1600mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time. D) Aqueous phase concentrate of iron as a function of time.

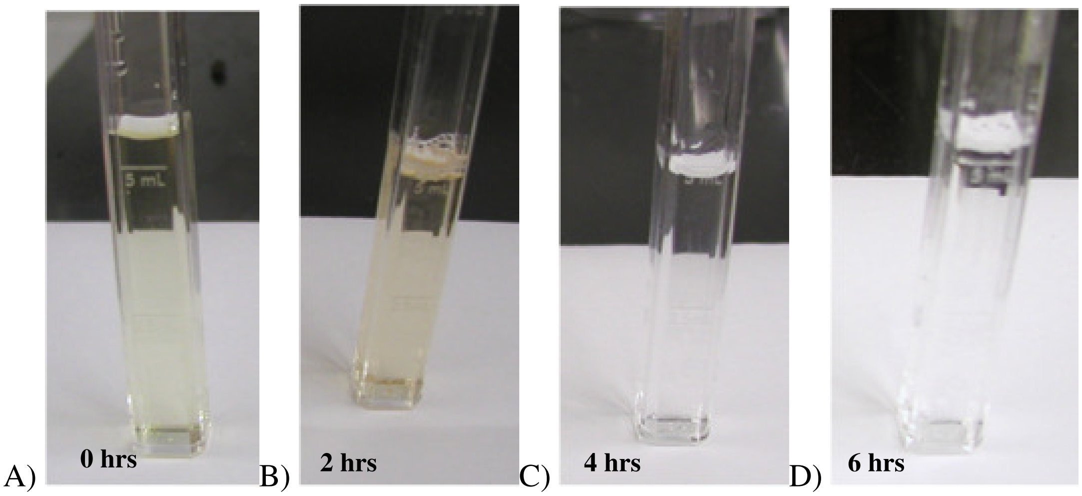


Figure 28. Qualitative measurement of iron(II) in solution at an applied potential of -1600mV after A) 0 hours, B) 2 hours, C) 4 hours, and D) 6 hours of electrolysis. A darker color correlates to a greater amount of iron(II) in solution.

Applied Potential of -1800mV (Figures 29 and 30)

For the applied potential of -1800mV, the experiment was run for a total of 1.5 hours only. This is in contrast with the 6 hours used for the other examined potentials. The current remained around 100mA, which was abnormally low as compared to the baseline of 180mA. The significant changes in Eh and pH that were noted in the -1600mV applied potential were not replicated in this experiment. This could have been the result of the lower current obtained in comparison to the baseline current, or due to the fact that the applied potential needed to be maintained for a longer period of time before significant changes could be seen in the bulk Eh and pH. For one replicate, the Eh decreased from 825mV to 524mV, and the pH increased from 2.5 to 4.2. This was not observed for the second replicate. The results of the amount of aqueous iron in solution had poor reproducibility, and only one replicate showed a significant decrease in iron from 480mg/L to 5mg/L, which confirmed that iron precipitated out. These results are shown in Figure 29.

The amount of iron(II) increased in solution from less than 0.5ppm to 1-2ppm after 1 hour of applied potential (Figure 30). After 1 hour, an iron precipitate was seen in the electrolytic cell. This precipitate corresponded to the results of the qualitative test (the solution became colorless suggesting a decrease in iron(II) in solution).

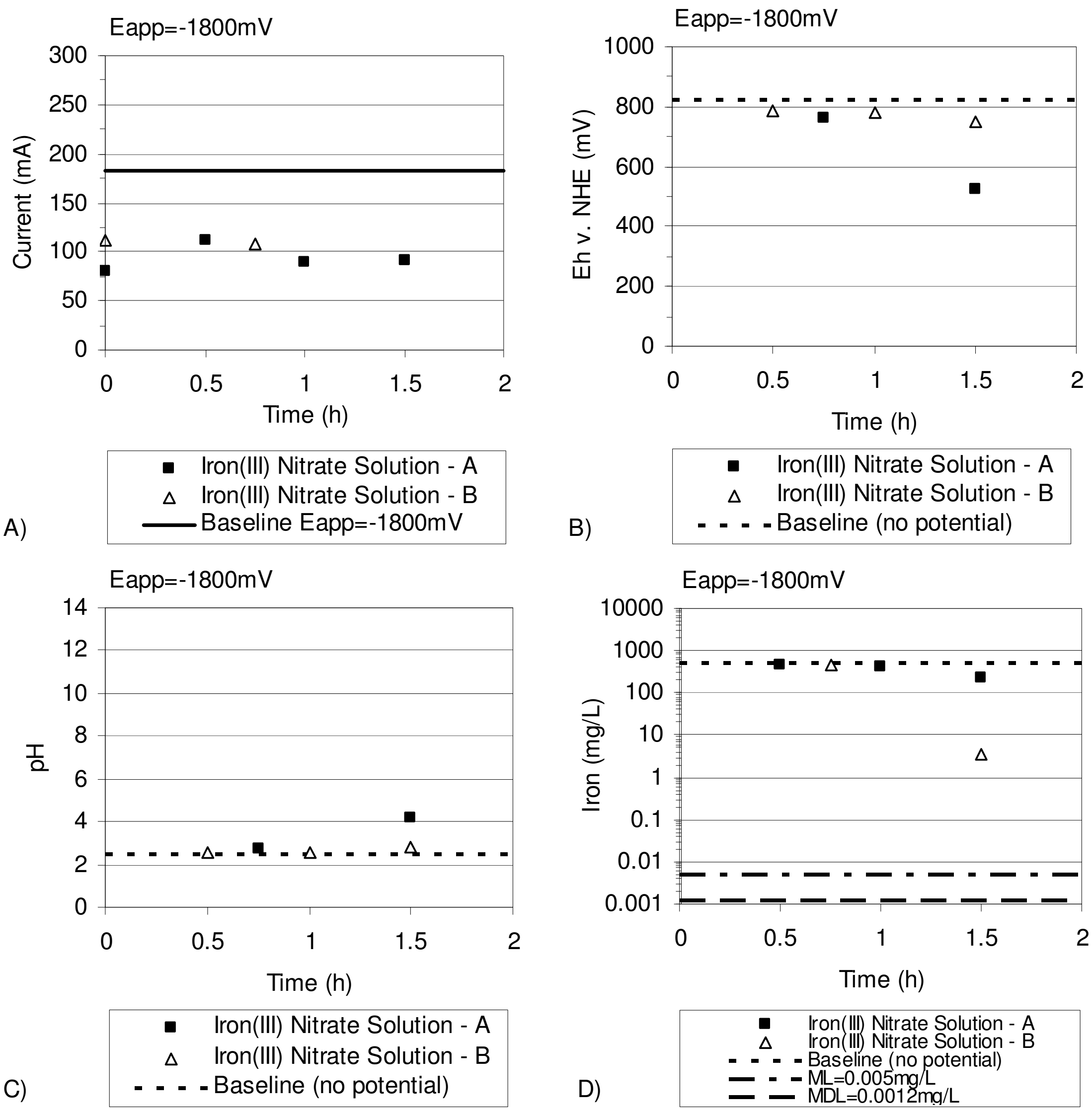


Figure 29. Electrolysis of a 0.01M iron(III) nitrate solution at an applied potential of -1800mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time. D) Aqueous phase concentrate of iron as a function of time.

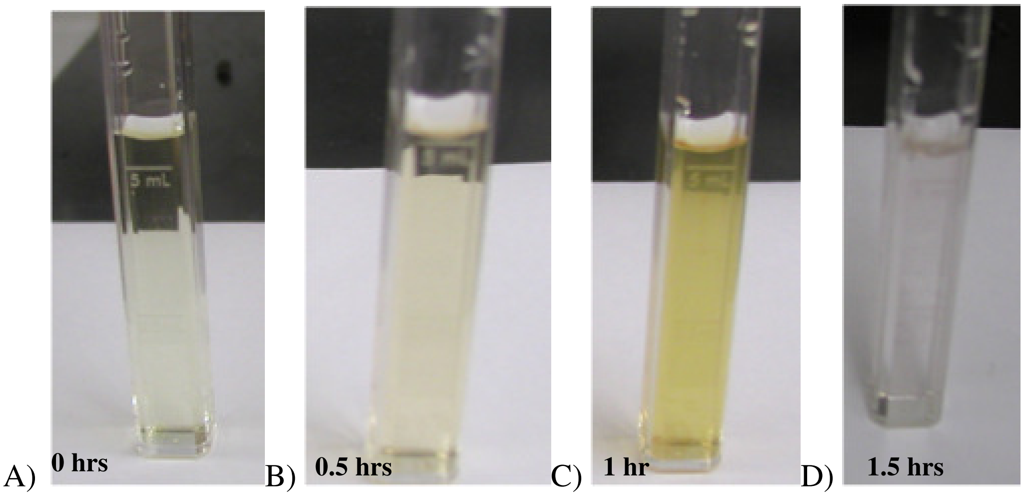


Figure 30. Qualitative measurement of iron(II) in solution at an applied potential of -1800mV after A) 0 hours, B) .5 hours, C) 1 hour, and D) 1.5 hours of electrolysis. A darker color correlates to a greater amount of iron(II) in solution.

Arsenic Contaminated Soil

For the arsenic contaminated soil, applied potentials of 0, -1200, -1400, -1600, and -1800mV were examined. For 0mV, the potential was applied for 1.5 hours, whereas the potential was applied for 6 hours total for other remaining potentials.

For each applied potential, two sets of graphs are presented. In the first set, figures A, B, and C show the current, solution Eh, and solution pH, respectively, as a function of time. In the second set, figures A, B, and C show the concentration of iron, arsenic, and copper as a function of time, respectively. For the applied potentials of -1400 and -1600mV, photographs depicting qualitative changes in the amount of iron(II) in solution are presented.

Applied potential of 0mV (Figures 31 and 32)

At the applied potential of 0mV, the current remained around the baseline current of 0.1mA. After 1.5 hours, the maximum decrease in measured Eh was from 323mV to 286mV, and the maximum increase in pH was from 6.6 to 7.0. These results are presented in Figure 31. The concentration of iron and copper in solution remained around 6mg/L and 0.09mg/L, respectively. A small increase in the amount of arsenic from the baseline of 1.3mg/L to 7.3mg/L was seen. The iron, arsenic, and copper results are presented in Figure 32. The qualitative iron(II) test was not sensitive enough to detect a change of iron(II) in solution at the applied potential of 0mV.

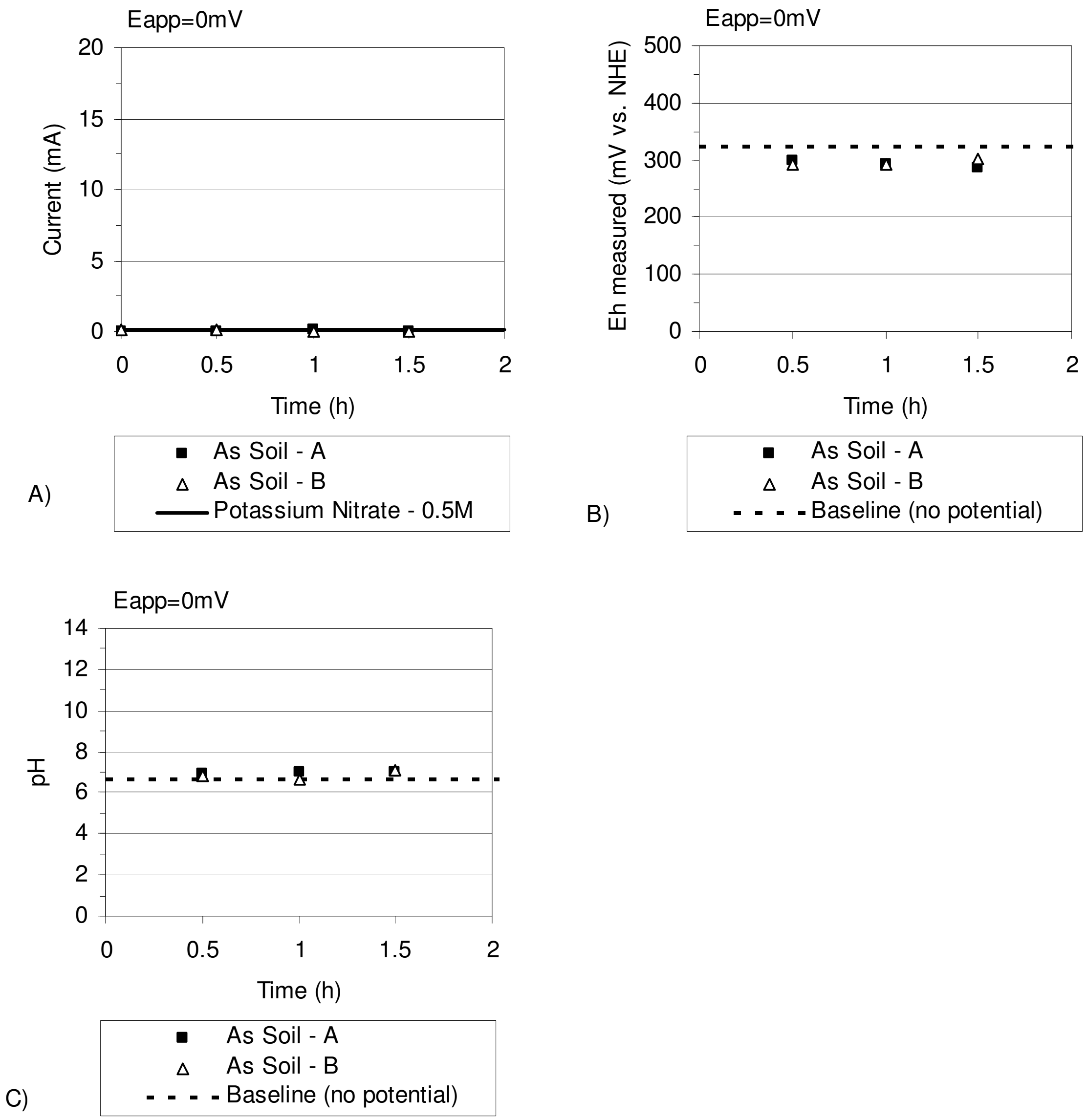


Figure 31. Electrolysis of a suspension of an arsenic contaminated soil at an applied potential of 0mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.

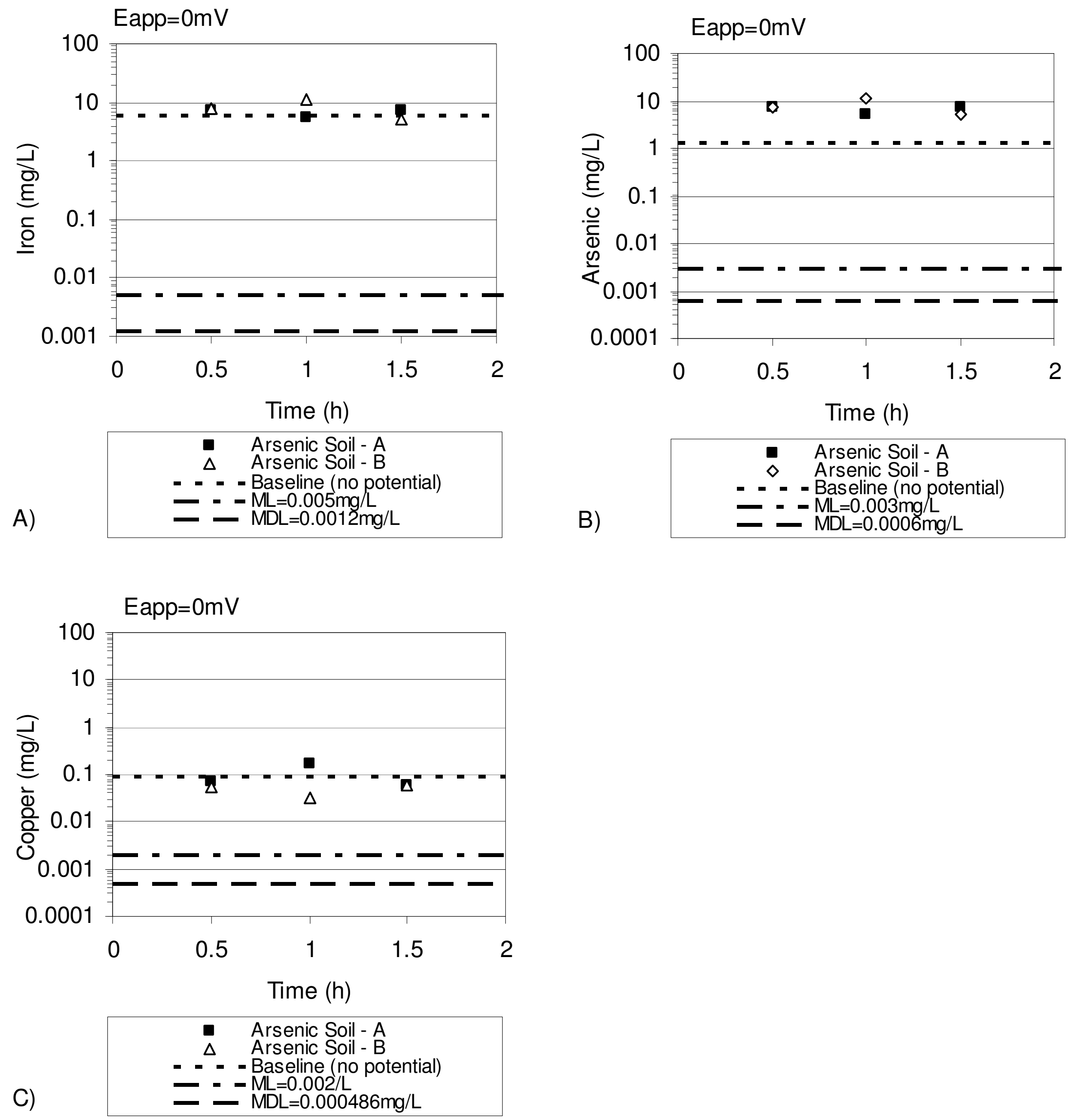


Figure 32. Electrolysis of a suspension of an arsenic contaminated soil at an applied potential of 0mV. A) Aqueous phase concentration of iron as a function of time. B) Aqueous phase concentration of arsenic as a function of time. C) Aqueous phase concentration of copper as a function of time.

Applied potential of -1200mV (Figures 33 and 34)

At the applied potential of -1200mV, poor replication was observed between the two replicates. For the first replicate, the current ranged from 7.9 to 5.8mA, whereas the second replicate had a current that remained around the baseline current (current of the electrolyte solution alone) of 2mA. Changes in the bulk pH and Eh of the soil suspension were observed. The Eh decreased from 323mV to as low as 173mV after 6 hours of electrolysis. The pH was increased from the baseline value of 6.6 to as high as 8.3. These results are presented in Figure 33. The aqueous concentration of iron, copper, and arsenic also showed poor reproducibility. Replicate B showed that the iron concentration was decreased from 6mg/L to 1.7mg/L after 6 hours, while replicate A showed little variation from the baseline. Replicate B also showed an increase in the amount of arsenic in solution from 1.3 to 4.2mg/L, which was more significant than the increase of 0.5mg/L shown in replicate A. The amount of copper in solution was stable throughout the experiment. These results are presented in Figure 34. At an applied potential of -1200mV, the qualitative test was not sensitive enough to detect the amount of iron(II) in solution.

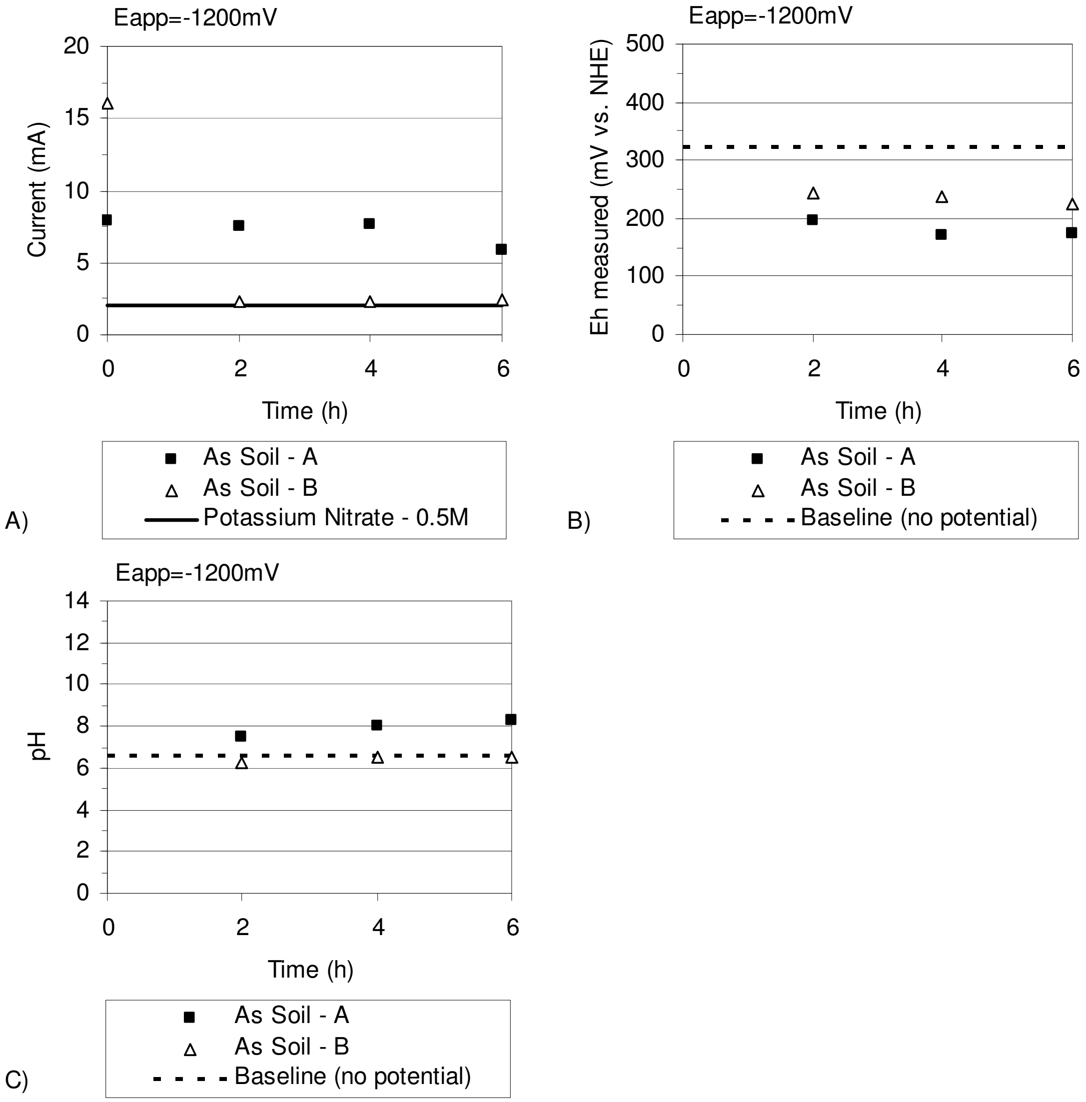


Figure 33. Electrolysis of a suspension of an arsenic contaminated soil at an applied potential of -1200mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.

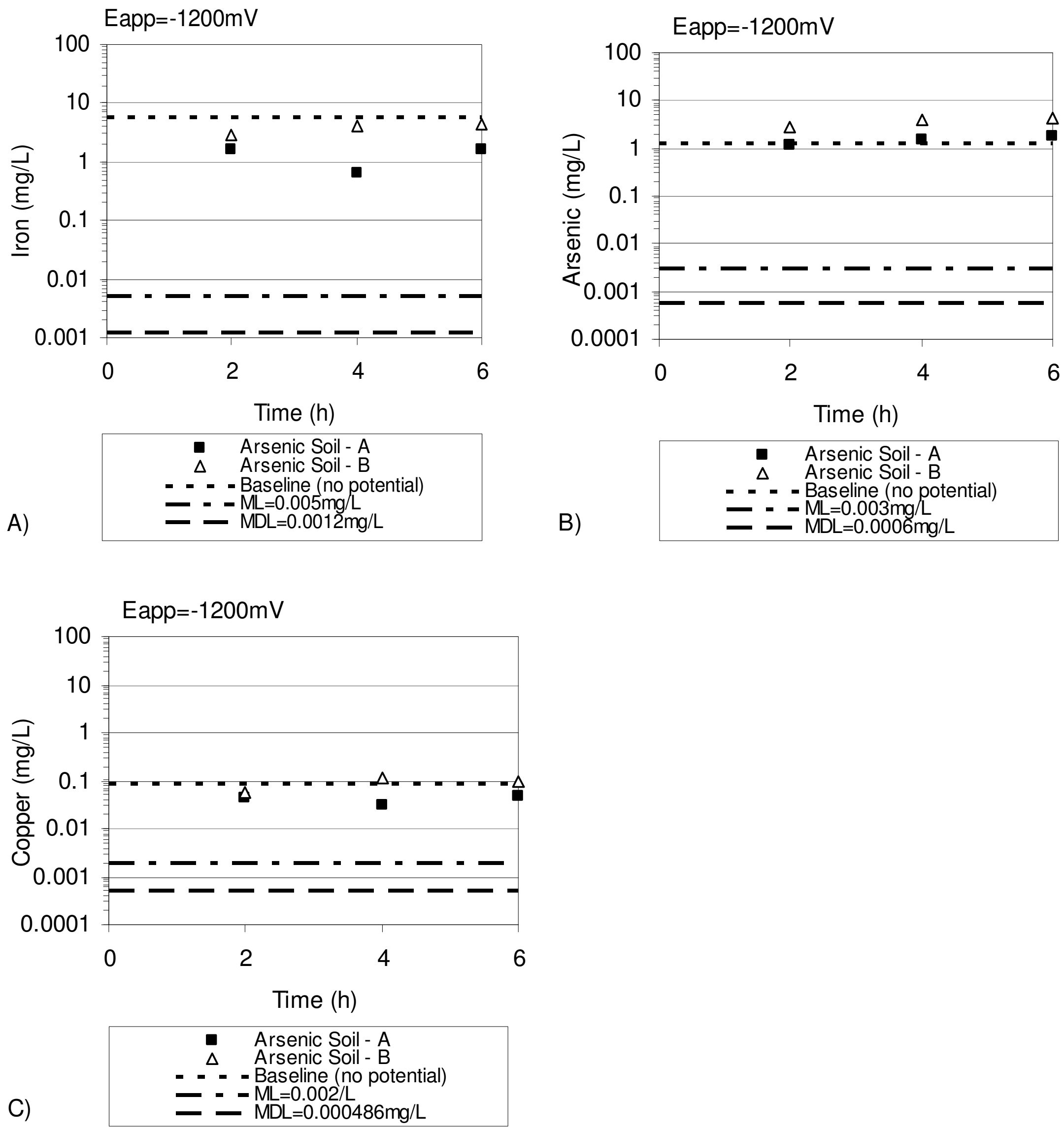


Figure 34. Electrolysis of a suspension of an arsenic contaminated soil at an applied potential of -1200mV. A) Aqueous phase concentration of iron as a function of time. B) Aqueous phase concentration of arsenic as a function of time. C) Aqueous phase concentration of copper as a function of time.

Applied potential of -1400mV (Figures 35-37)

At the applied potential of -1400mV, overall good reproducibility was obtained for the current, pH, and bulk measured Eh. The current remained around 44mA throughout the 6 hour experiment, which was significantly above the baseline current of 4.2mA. Significant changes were seen in the measured Eh and pH of the bulk solution. The measured Eh decreased from 323mV to 99mV over a 6 hour period. The pH increased from 6.6 to 11.3 over the same time frame. These results are presented in Figure 35. The aqueous concentrations of iron and arsenic showed poor reproducibility. Replicate A showed that the iron concentration was increased from 6mg/L to 15.4mg/L after 6 hours, while replicate B showed little change from the baseline. Replicate A also showed a larger increase in the amount of arsenic in solution from 1.3 to 5mg/L, which was more significant than the increase of 1mg/L obtained in replicate B. The amount of copper in solution was doubled in both replicates from 0.09mg/L to 0.183mg/L. These results are presented in Figure 36. The qualitative test showed that the baseline solution was clear and colorless, whereas after 2 hours the color change was a light yellow corresponding to a concentration of iron(II) of about 0.5mg/L (Figure 37). However, the color intensity of the solution did not increase over time, which suggested that the test was either not sensitive enough, or that the amount of iron(II) had stabilized in solution after 2 hours of applied potential.

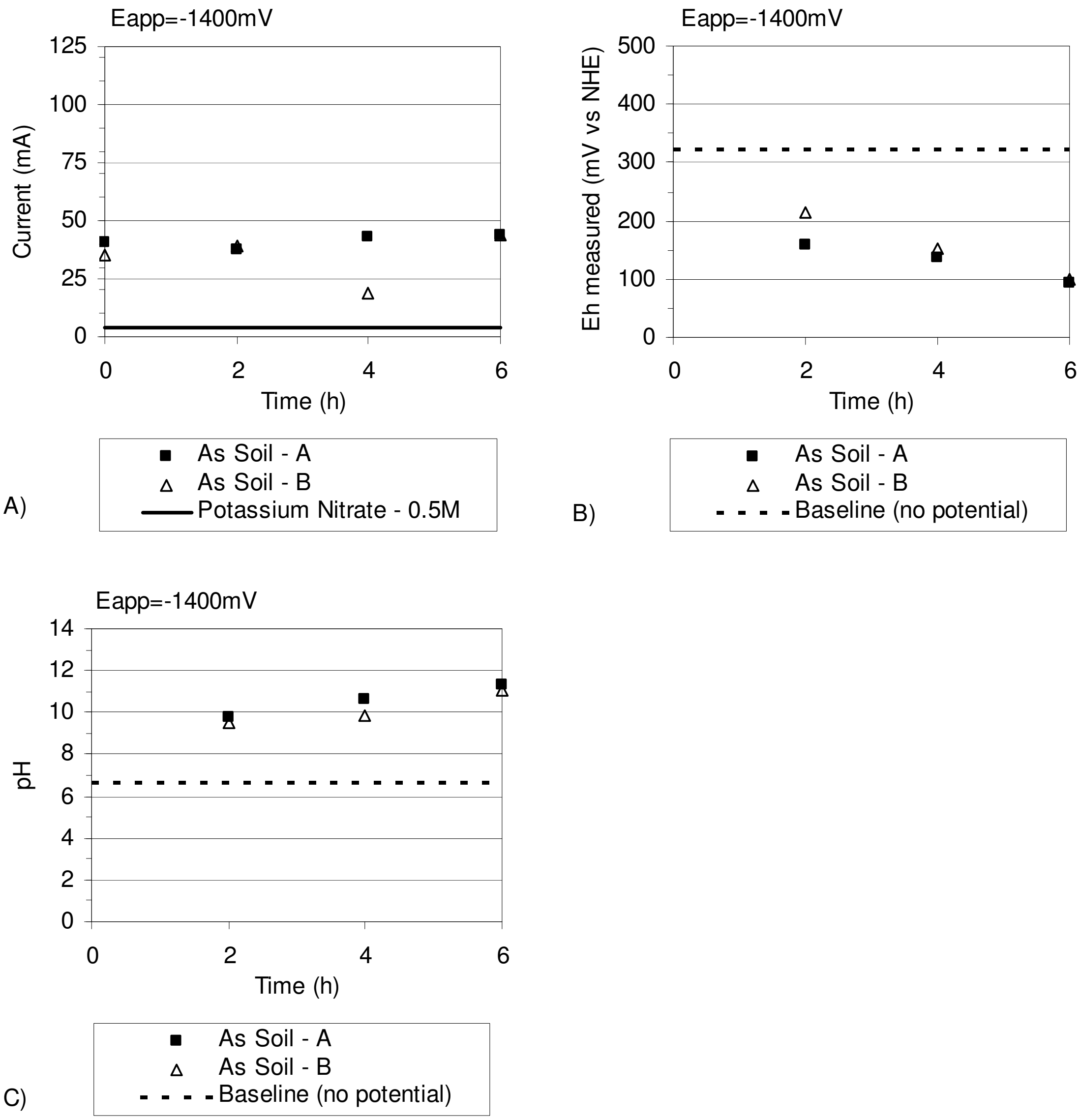


Figure 35. Electrolysis of a suspension of an arsenic contaminated soil at an applied potential of -1200mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.

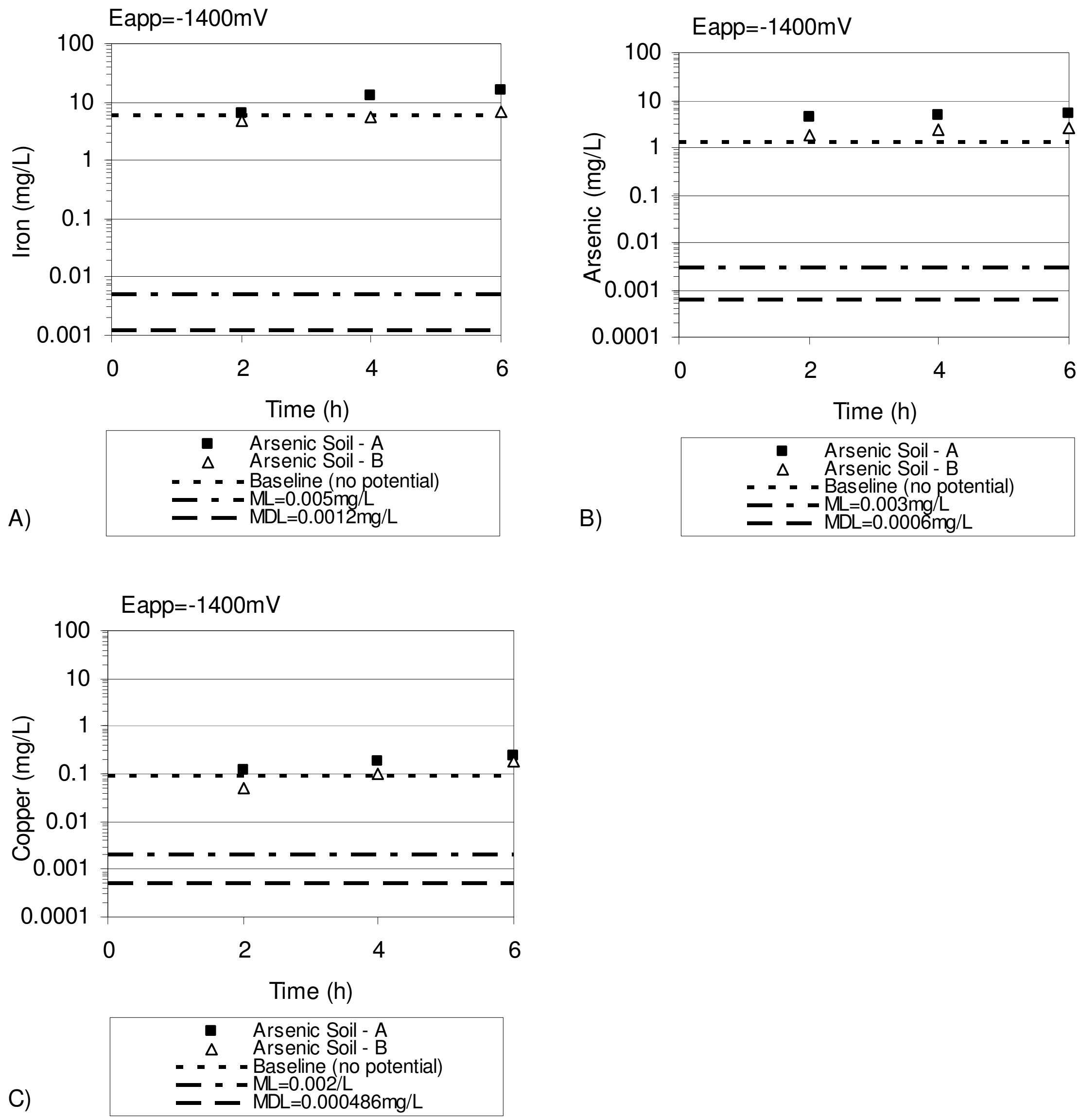


Figure 36. Electrolysis of a suspension of an arsenic contaminated soil at an applied potential of -1200mV. A) Aqueous phase concentration of iron as a function of time. B) Aqueous phase concentration of arsenic as a function of time. C) Aqueous phase concentration of copper as a function of time.

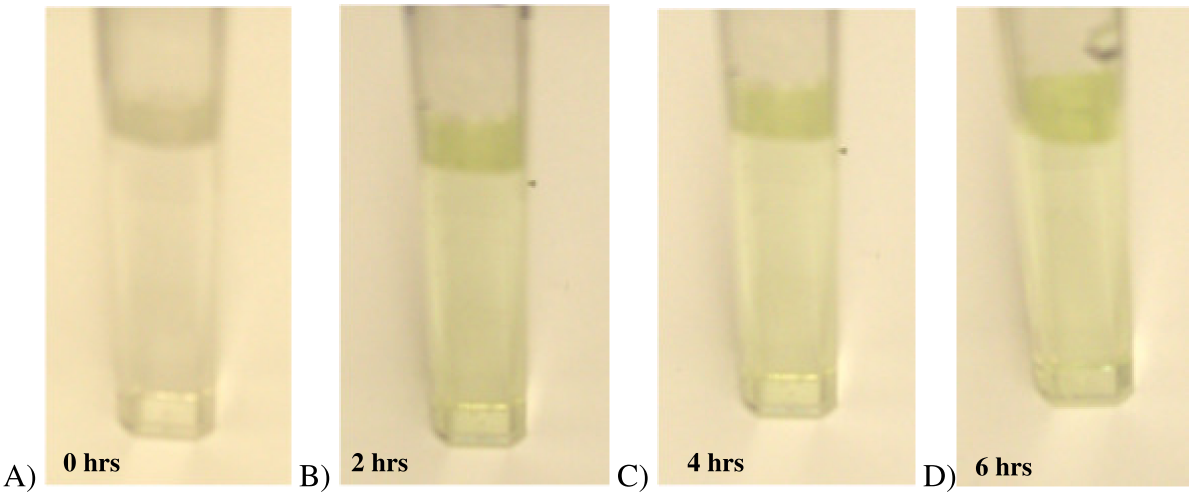


Figure 37. Qualitative measurement of iron(II) in solution at an applied potential of -1400mV after A) 0 hours, B) 2 hours, C) 4 hours, and D) 6 hours of electrolysis. A darker color correlates to a greater amount of iron(II) in solution.

Applied potential of -1600mV (Figures 38-40)

At the applied potential of -1600mV, poor reproducibility of the current was observed. The current remained around 127mA for replicate A for the duration of the experiment (6 hours), which was significantly above replicate B that remained around the baseline of 50mA. Significant changes were seen in the measured Eh and pH of the bulk solution. The measured Eh decreased from 323mV to as low as 50mV after 6 hours of electrolysis. This was 50mV lower than was seen when the applied potential of -1400mV was used. The pH increased from 6.6 to 12.2 over the same time frame, which again was higher than the final pH value of 11.3 when -1400mV was applied. These results are presented in Figure 38. The aqueous concentrations of iron, arsenic, and copper showed poor reproducibility. The iron data showed a slight increase in the amount in solution from 6 to as high as 13.6mg/L. The arsenic data was divergent with one replicate showing an increase of 2mg/L, while the second replicate showed a decrease in the amount of arsenic from 1.3 to 0.3mg/L. The copper data also was dissimilar with one replicate hovering around the baseline value, whereas the other replicate showed an increase from 0.09mg/L to 0.262mg/L. These results are presented in Figure 39. The qualitative test for iron(II) showed that the baseline solution was clear and colorless, whereas after 2 hours the color change was a light yellow corresponding to a concentration of iron(II) of about 0.5mg/L (Figure 40). The results mirrored the qualitative data from the experiment at an applied potential of -1400mV.

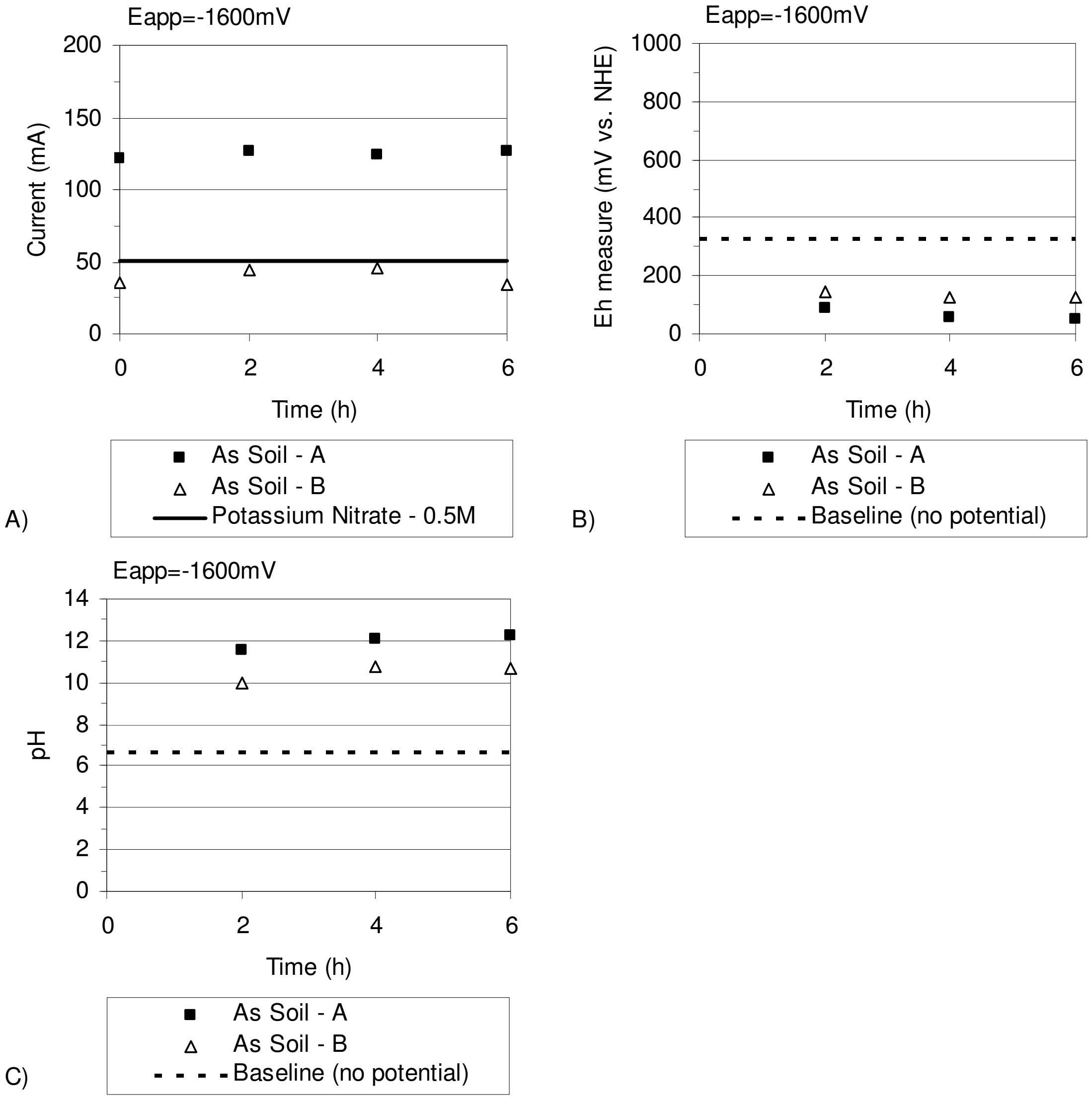


Figure 38. Electrolysis of a suspension of an arsenic contaminated soil at an applied potential of -1600mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.

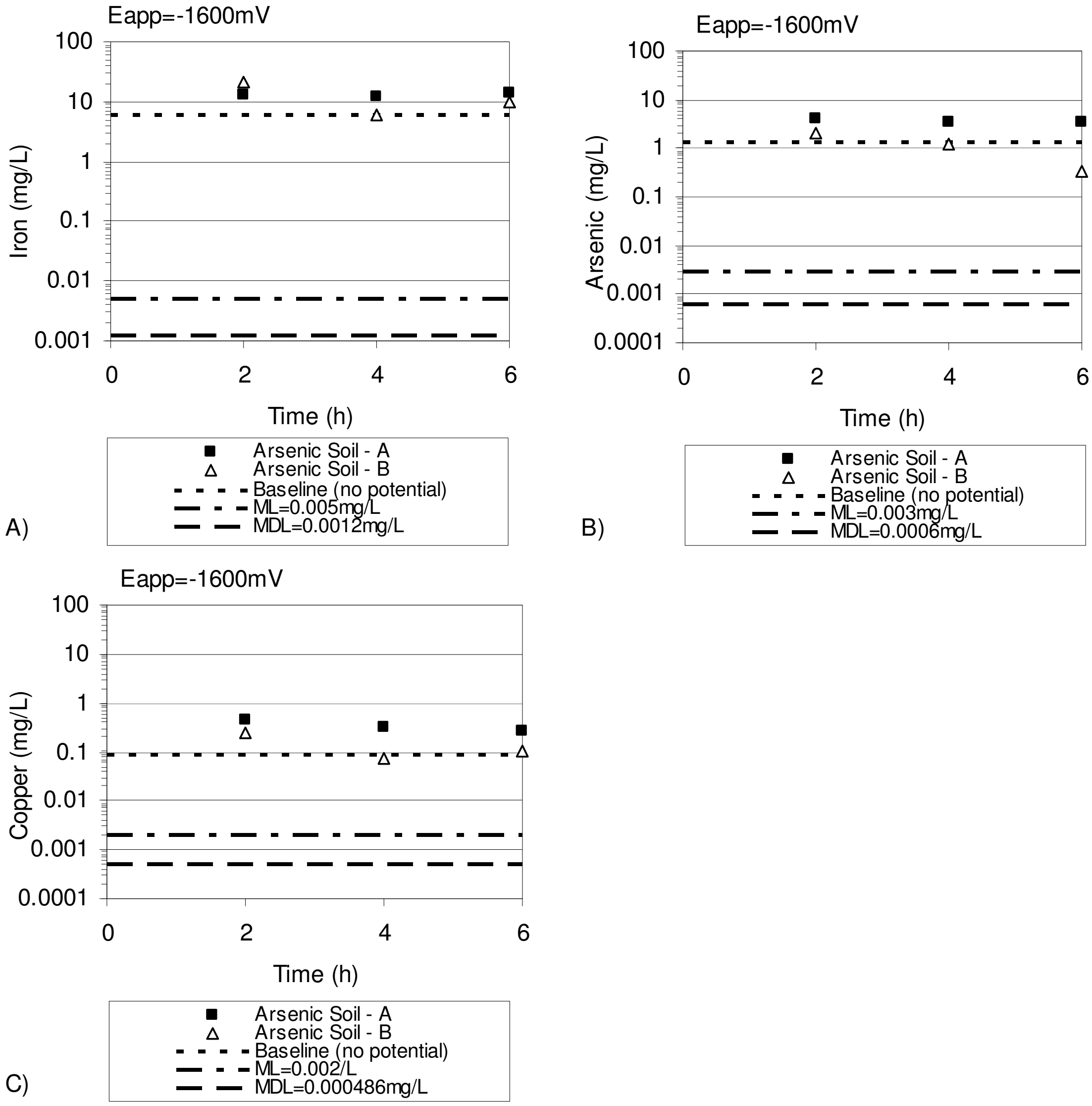


Figure 39. Electrolysis of a suspension of an arsenic contaminated soil at an applied potential of -1600mV. A) Aqueous phase concentration of iron as a function of time. B) Aqueous phase concentration of arsenic as a function of time. C) Aqueous phase concentration of copper as a function of time.

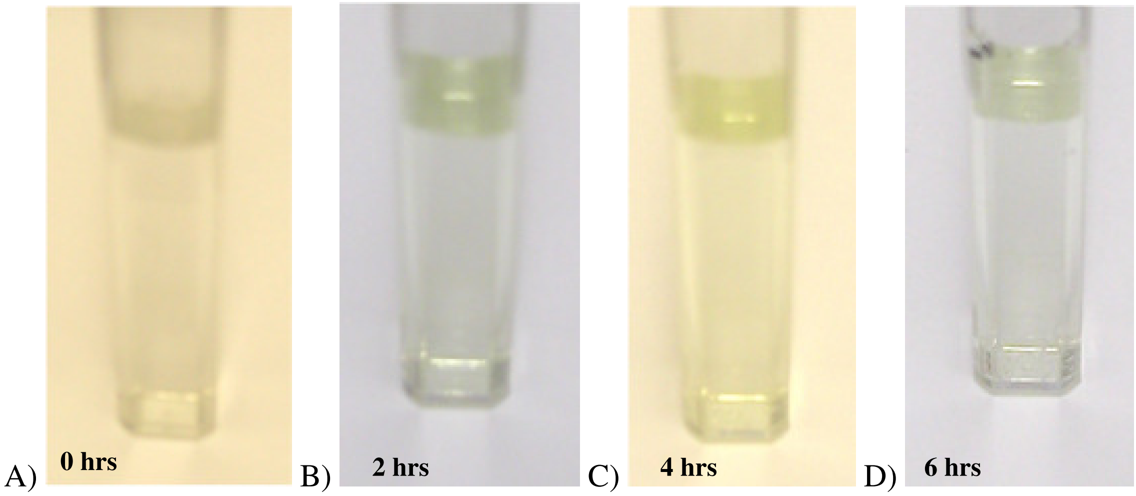


Figure 40. Qualitative measurement of iron(II) in solution at an applied potential of -1600mV after A) 0 hours, B) 2 hours, C) 4 hours, and D) 6 hours of electrolysis. A darker color correlates to a greater amount of iron(II) in solution.

Applied potential of -1800mV (Figures 41 and 42)

At the applied potential of -1800mV, the current showed an initial increase before beginning to decrease after 4 hours of electrolysis. The current remained at least 36mA above the baseline of 50mA at all times. As in the case of -1400 and -1600mV applied potentials, significant changes were seen in the measured Eh and pH of the bulk solution. The measured Eh decreased from 323mV to 16.5mV after 6 hours of electrolysis. This was 35mV lower than was seen when the applied potential of -1600mV was used. The pH increased from 6.6 to as high as 12.7 over the same time frame, which was slightly higher than the final pH value of 12.3 when -1600mV was applied. These results are presented in Figure 41. The iron data showed a slight increase 6mg/L to as high as 21mg/L, which was more than was in solution after 6 hours at an applied potential of -1600mV. The arsenic data showed an increase from 1.3 to 3.3mg/L, which is the same amount of arsenic that was in solution for replicate A at an applied potential of -1600mV.

The copper data showed an increase from 0.090mg/L to 0.432mg/L. These results are presented in Figure 42. The qualitative test for iron(II) showed that the baseline solution was clear and colorless, whereas after 2 hours the color change was a light yellow corresponding to a concentration of iron(II) of about 0.5mg/L. The color intensity of the test did not show an increase for extracts obtained at times greater than 2 hours of electrolysis. These results mirrored the qualitative data from the experiment at -1400 and -1600mV applied potential.

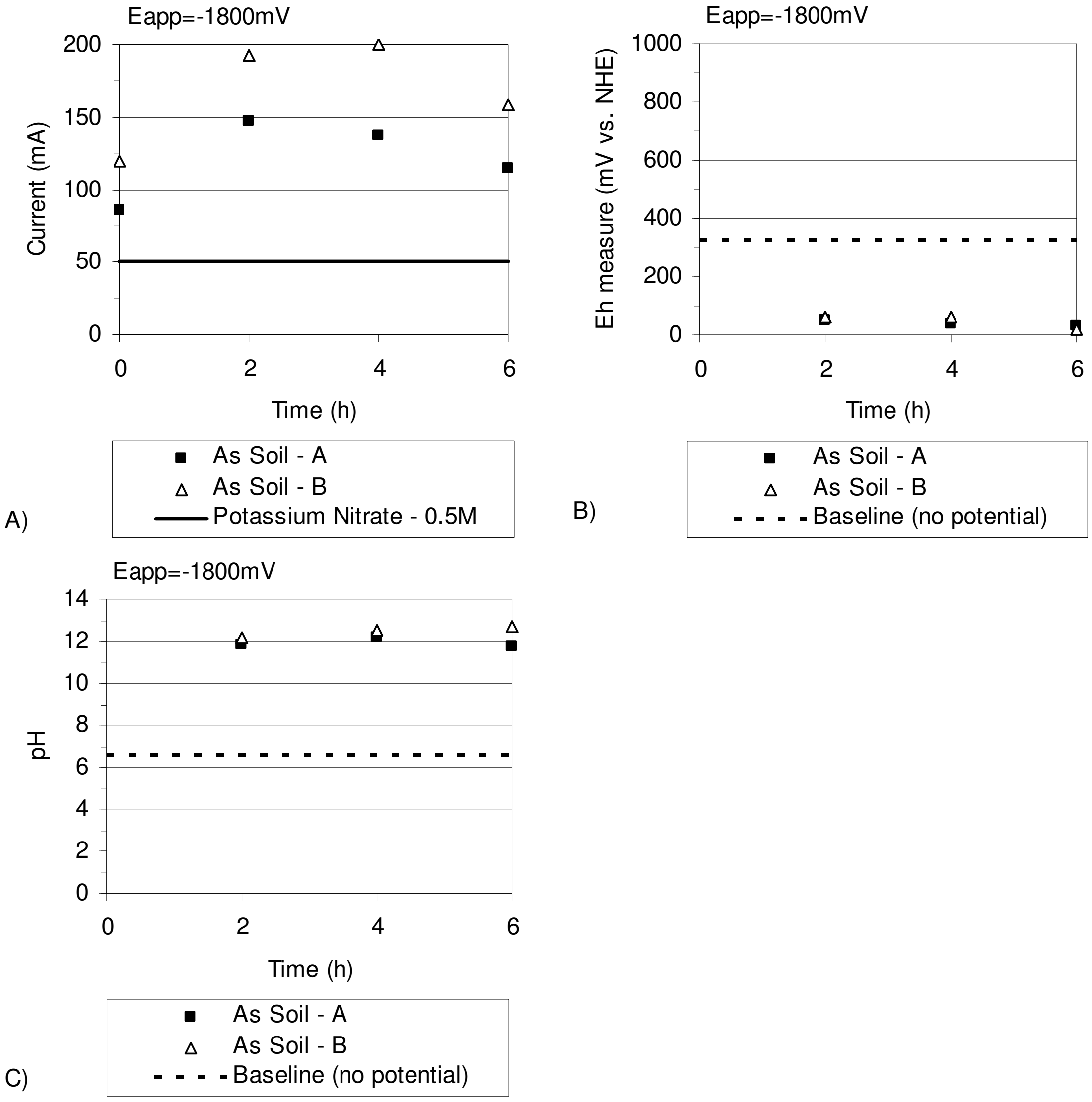


Figure 41. Electrolysis of a suspension of an arsenic contaminated soil at an applied potential of -1800mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.

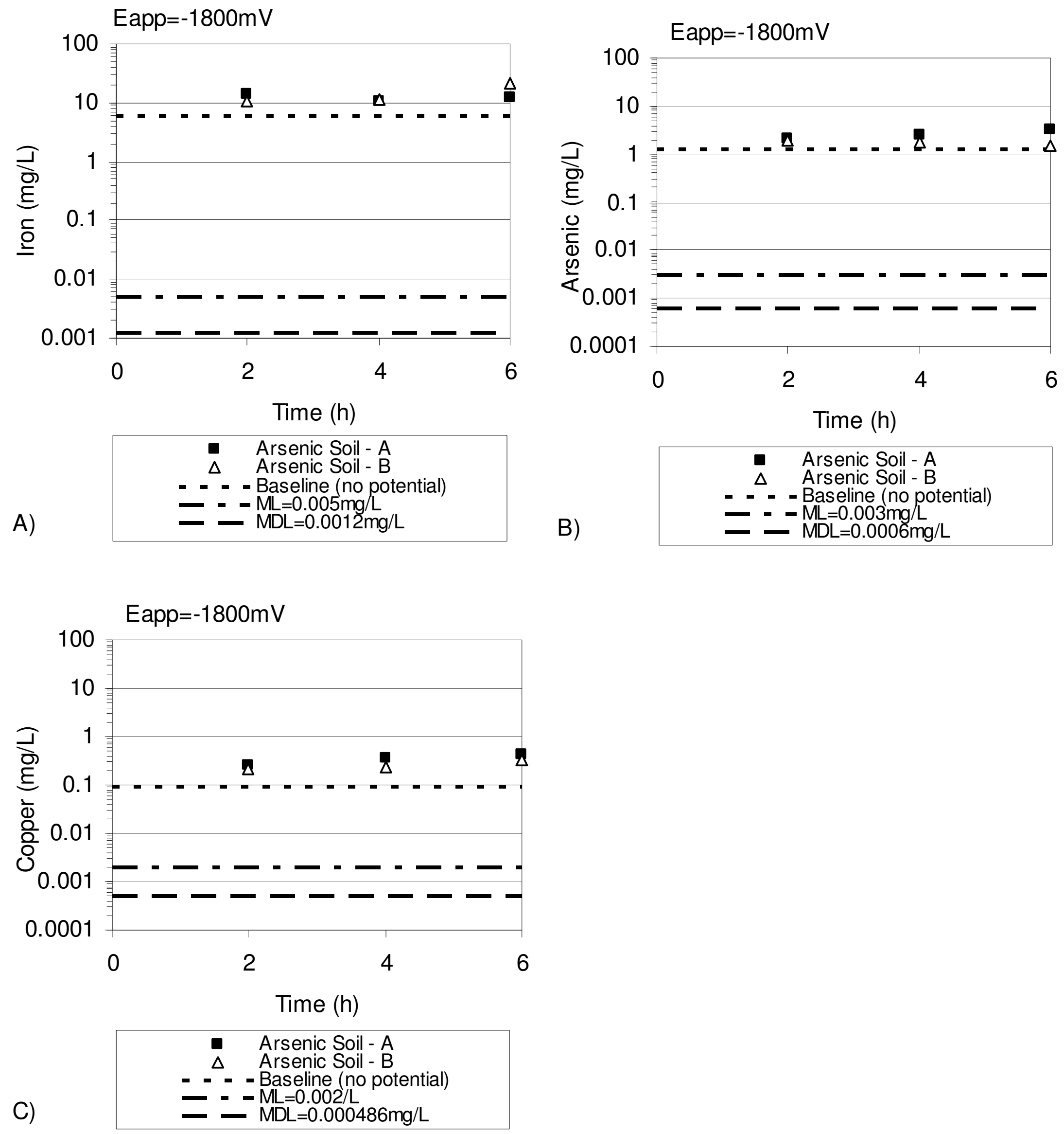


Figure 42. Electrolysis of a suspension of an arsenic contaminated soil at an applied potential of -1800mV. A) Aqueous phase concentration of iron as a function of time. B) Aqueous phase concentration of arsenic as a function of time. C) Aqueous phase concentration of copper as a function of time.

Furnace Slag

For the furnace slag, applied potentials of 0, +1600, and +2000mV were examined. Two electrolyte solutions were used for each applied potential: 1) 0.5M potassium nitrate and 2) 0.05M EDTA. EDTA was tested as an electrolytic solution because of its chelating properties that result in an increase in the concentration of the constituents in solution and therefore was expected to increase the constituents' availability for electrolysis. No significant changes in the bulk solution Eh or pH were observed as a result of the electrolyte used. The concentrations of the constituents in solution for the electrolyte and furnace slag are presented in Table 5. No qualitative information on the amount of iron(II) in solution is available for the electrolysis experiments of the furnace slag as the test was unable to detect the amount of iron(II) in solution regardless of electrolyte used.

For each applied potential, four sets of figures are presented. In the first two sets of figures, figures A, B, and C present the current, solution Eh, and pH, respectively, for 0.5M potassium nitrate and 0.05M EDTA. In the second two sets of figures, Figures A, B, C, D, and E show the concentrations of iron, arsenic, copper, strontium, and barium, respectively, for 0.5M potassium nitrate and 0.05M EDTA.

Table 5. The concentration of constituents in solution from furnace slag in 0.5M potassium nitrate and 0.05M EDTA (no applied potential).

		Furnace Slag in 0.5M Potassium Nitrate (µg/L)	**Furnace Slag in 0.05M EDTA (µg/L)**
Iron	Fe	856	3977
Arsenice	As	4	1
Copper	Cu	15	18
Strontium	Sr	942	1307
Barium	Ba	804	176

Applied Potential of 0mV (Figures 43-46)

At the applied potential of 0mV, the current remained around the baseline current of 0mA. No changes were seen in the bulk measurements of the Eh or pH independent of the electrolyte solution used (potassium nitrate or EDTA). The Eh remained around -100mV and the pH remained around 12.6 in both cases. These results are presented in Figures 43 and 44 for potassium nitrate and EDTA, respectively. No significant change in iron, strontium, and barium concentrations could be observed over the entire duration of the electrolysis (6 hours). The iron concentration remained stable around a value of 856µg/L and 3980µg/L for the potassium nitrate and EDTA cases, respectively. Arsenic concentration was in all cases below the detection limits. The amount of copper in solution gradually decreased over the course of the experiment from 15µg/L to as low as below the detection limits when potassium nitrate was used; however, no trend was seen in the copper concentration when EDTA was used. These results are presented in Figures 45 and 46 for potassium nitrate and EDTA, respectively.

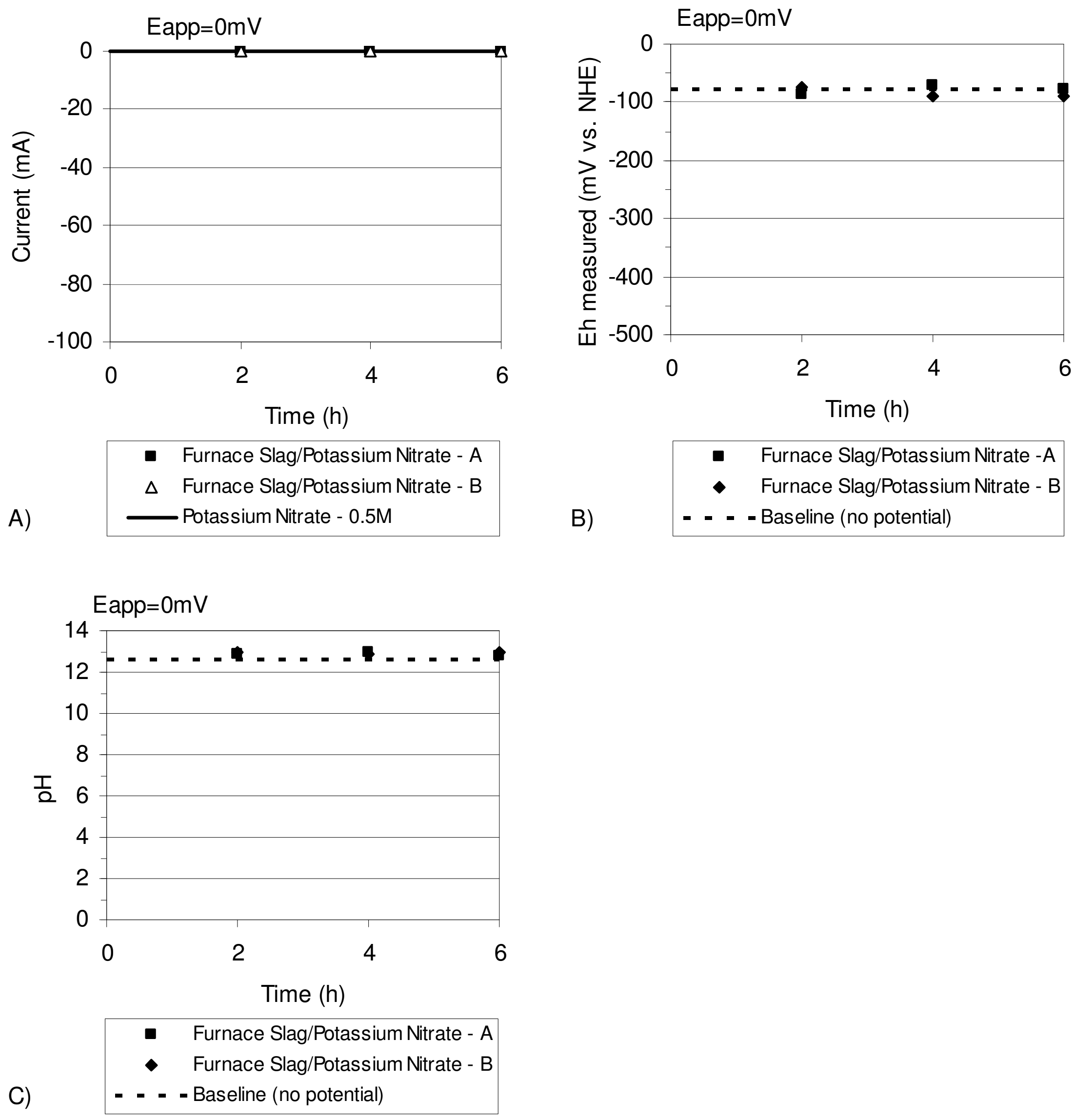


Figure 43. Electrolysis of a solution of furnace slag in 0.5M potassium nitrate at an applied potential of 0mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.

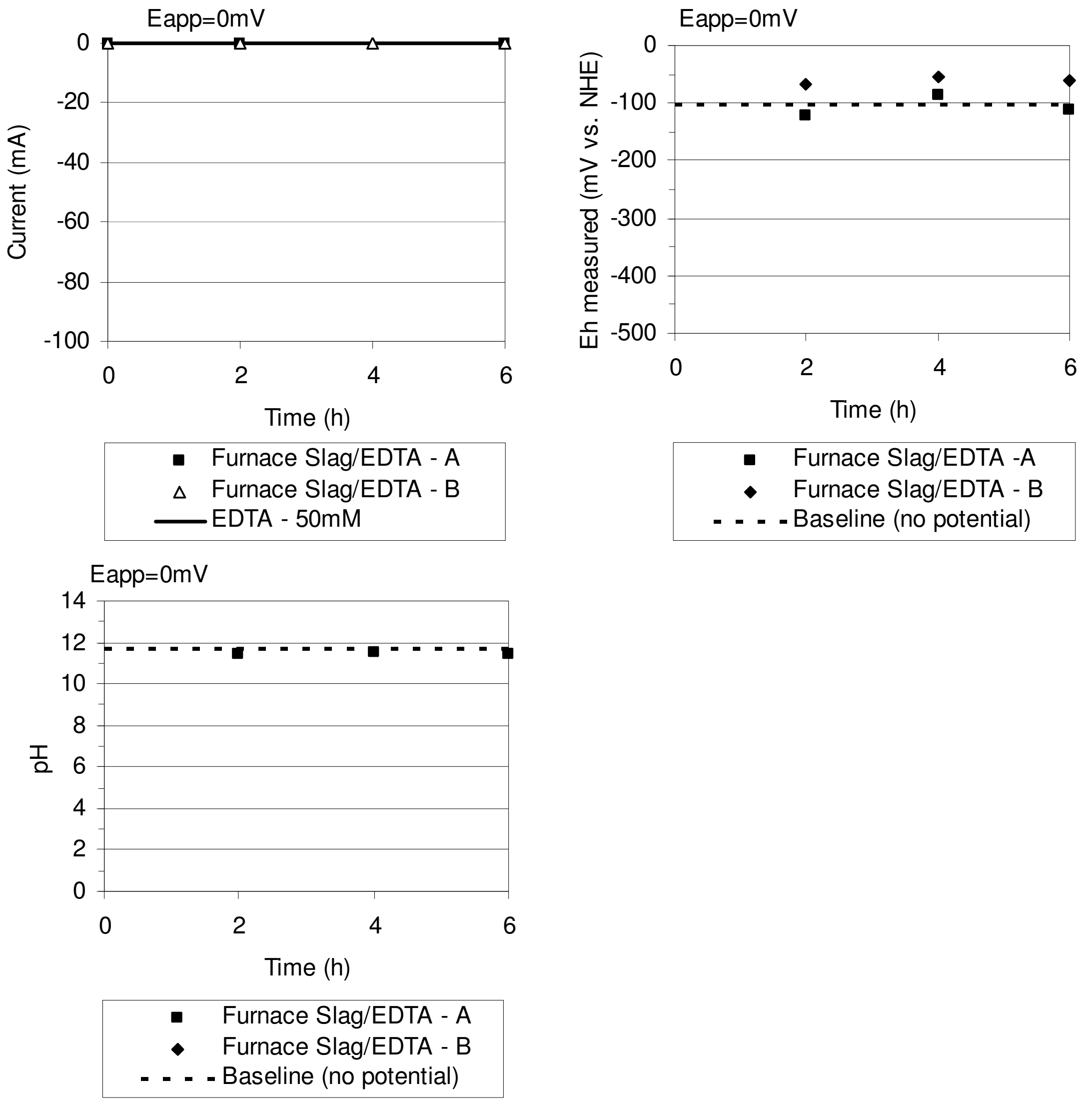


Figure 44. Electrolysis of a solution of furnace slag in 50mM EDTA at an applied potential of 0mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.

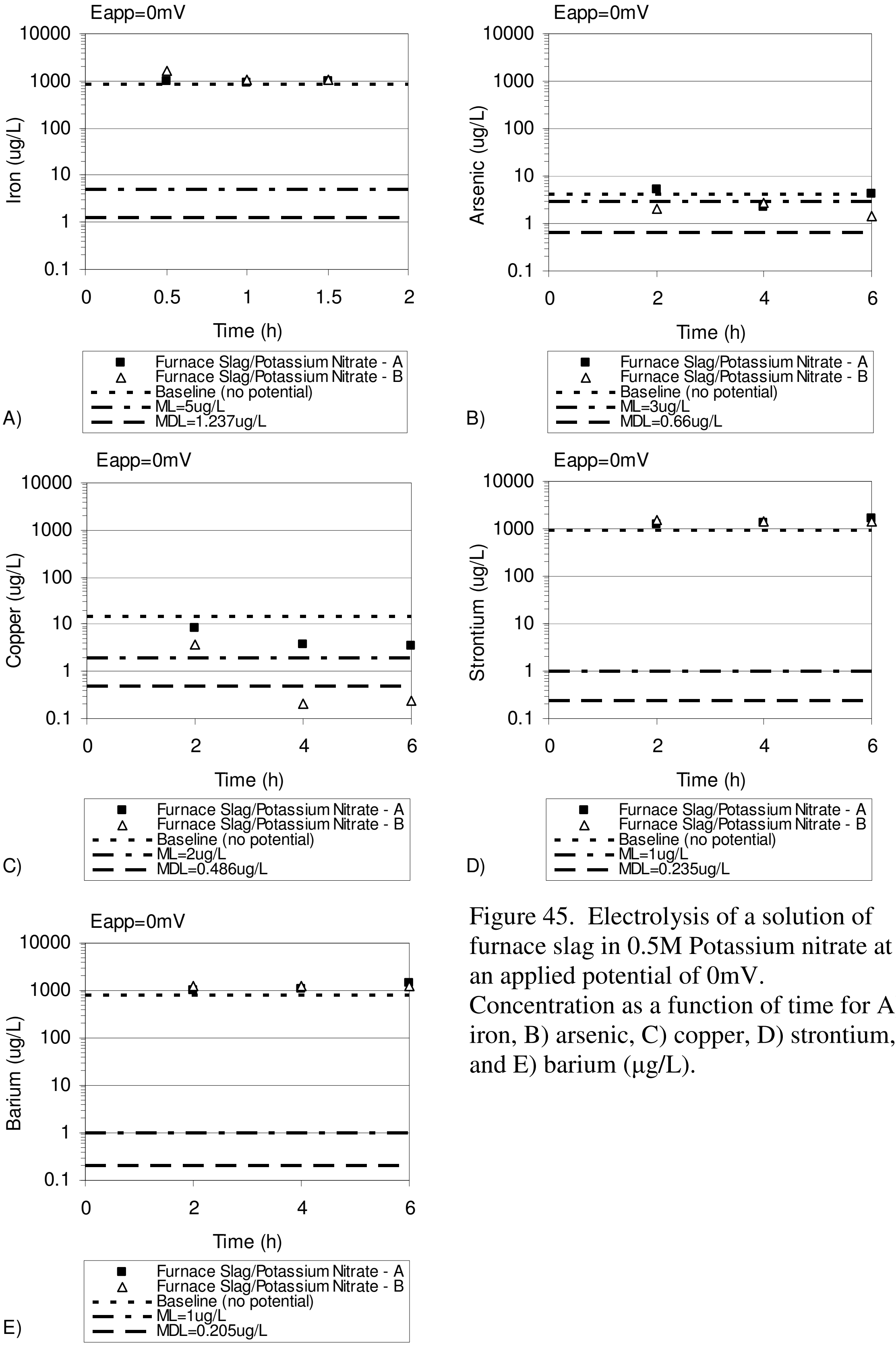
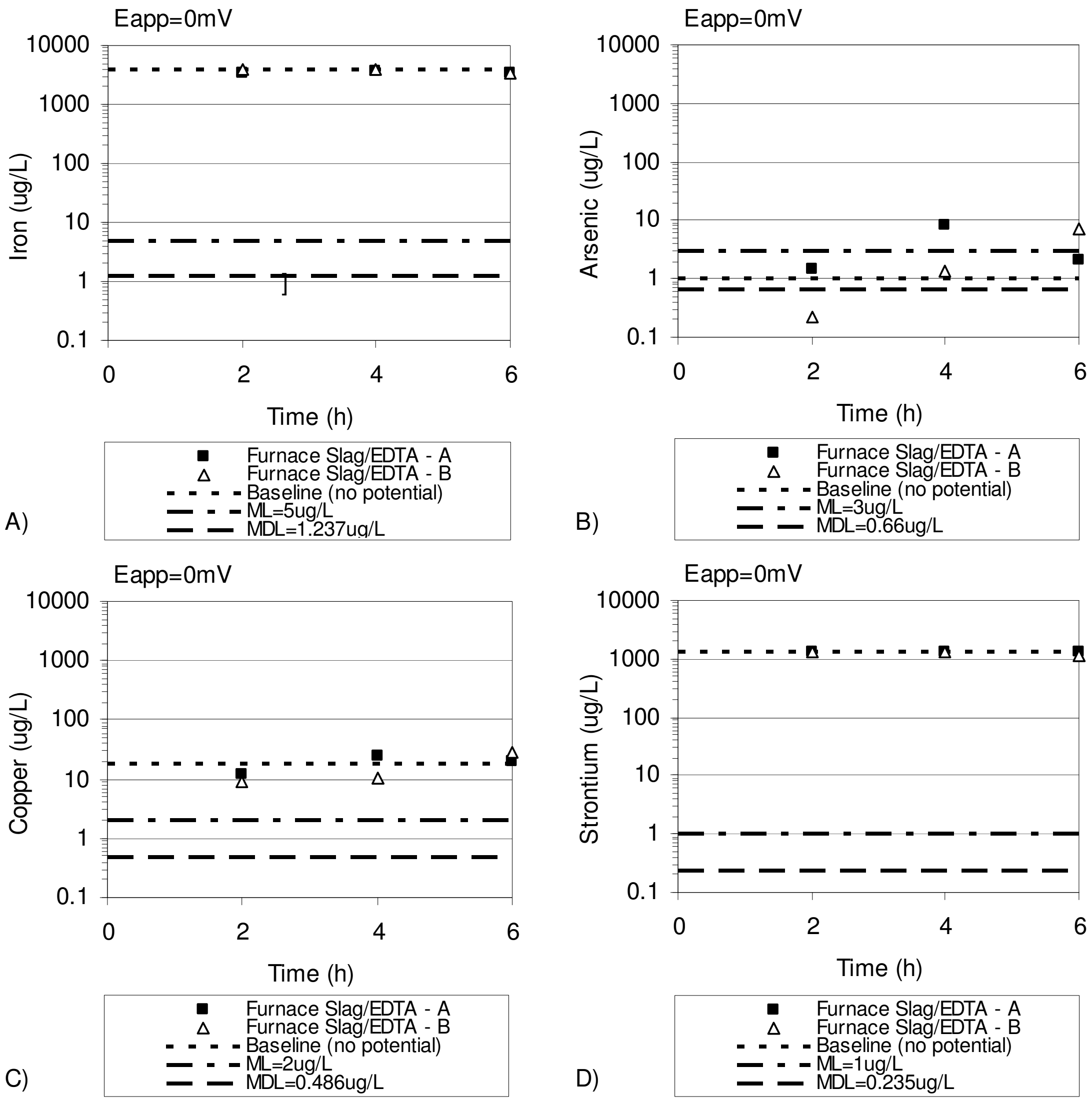


Figure 45. Electrolysis of a solution of furnace slag in 0.5M Potassium nitrate at an applied potential of 0mV. Concentration as a function of time for A) iron, B) arsenic, C) copper, D) strontium, and E) barium (µg/L).



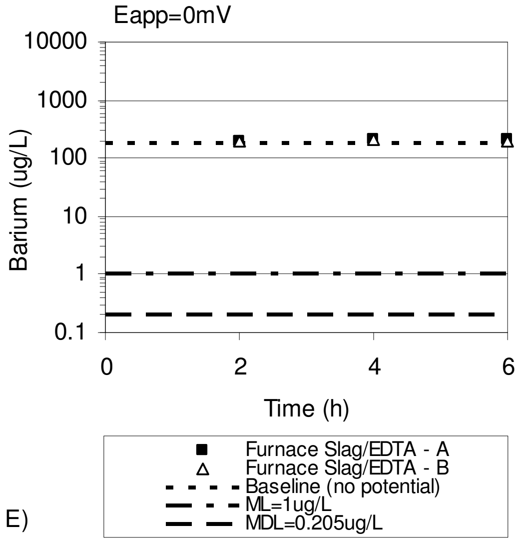


Figure 46. Electrolysis of a solution of furnace slag in 50mM EDTA at an applied potential of 0mV. Concentration as a function of time for A) iron, B) arsenic, C) copper, D) strontium, and E) barium (μg/L)

Applied Potential of +1600mV (Figures 47-50)

At the applied potential of +1600mV, the current was negative and remained around a value of -2mA. This is in contrast with the baseline values of -12mA and -33mA for the potassium nitrate and EDTA, respectively. No significant change in the bulk solution Eh could be observed when potassium nitrate was used as the electrolyte solution. In contrast, when EDTA was used as the electrolyte solution, a decrease in the bulk solution Eh was observed from a value of about -100 to a value of -200mV. These results seemed to indicate that the applied potential of +1600mV was not appropriate for oxidizing the suspension. During the electrolysis, no significant change in solution pH was observed for either electrolyte. These results are presented in Figures 47 and 48 for potassium nitrate and EDTA, respectively. The results of the concentration data showed that the amount of iron, strontium, and barium remained the same throughout the experiment for both potassium nitrate and EDTA. The arsenic data was inconclusive as several of the points were below the detection limits. As was seen at 0mV, the amount of copper in solution gradually decreased over the course of the experiment from 15 μg/L to 2μg/L when potassium nitrate was used, while it remained stable when EDTA was used as the electrolyte solution. These results are presented in Figures 49 and 50 for potassium nitrate and EDTA, respectively.

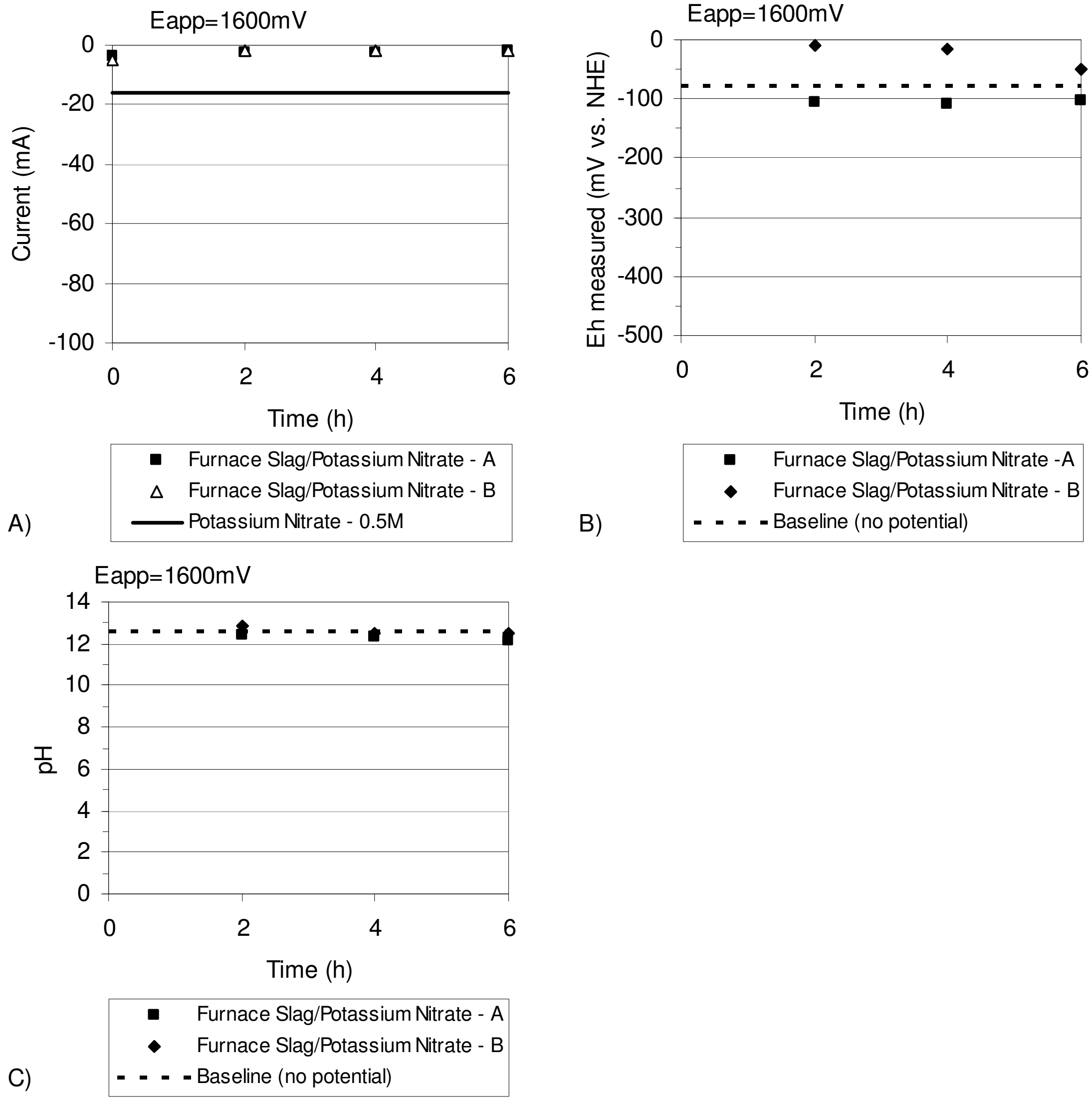


Figure 47. Electrolysis of a solution of furnace slag in 0.5M potassium nitrate at an applied potential of +1600mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.

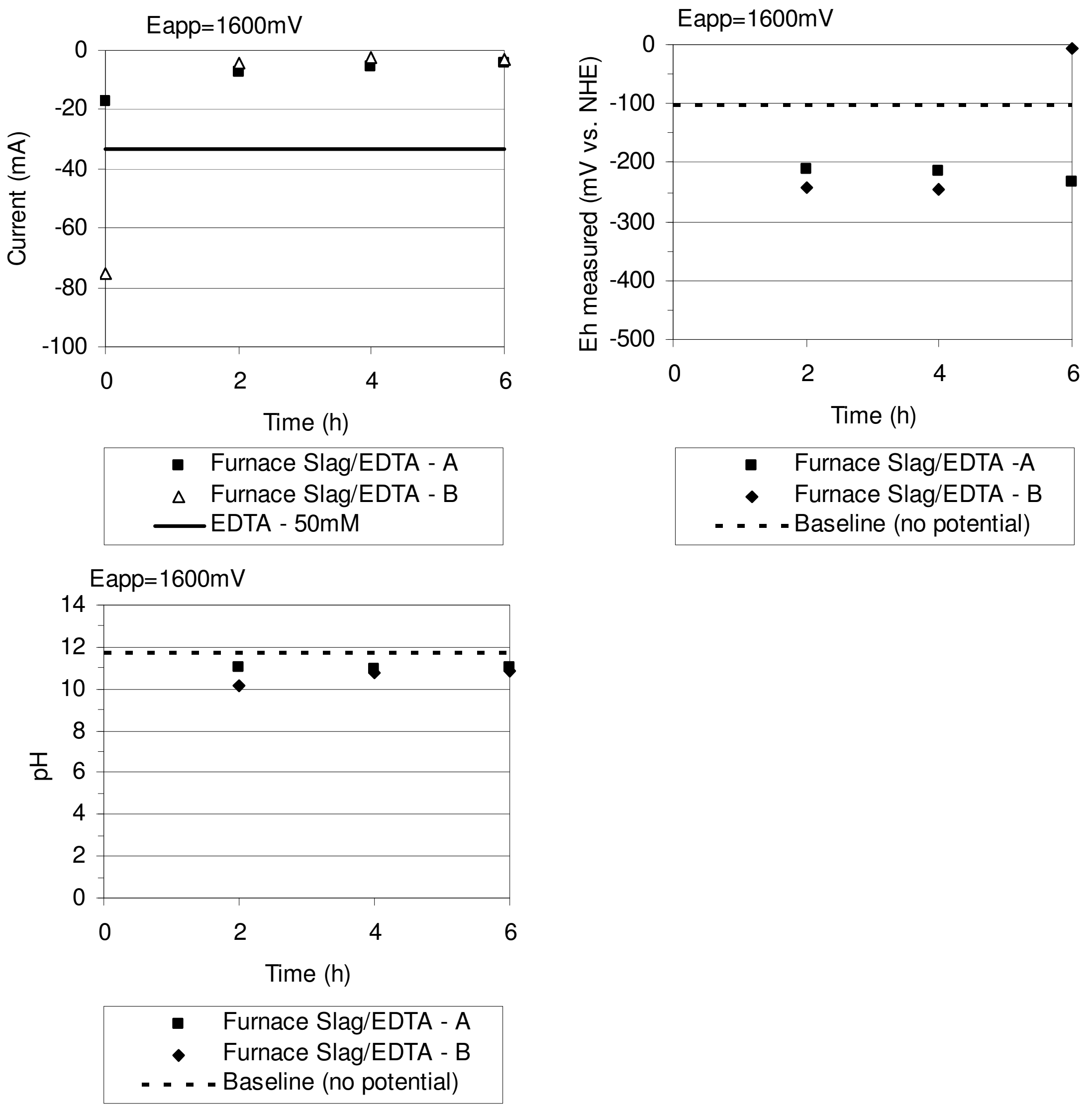


Figure 48. Electrolysis of a solution of furnace slag in 50mM EDTA at an applied potential of +1600mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.

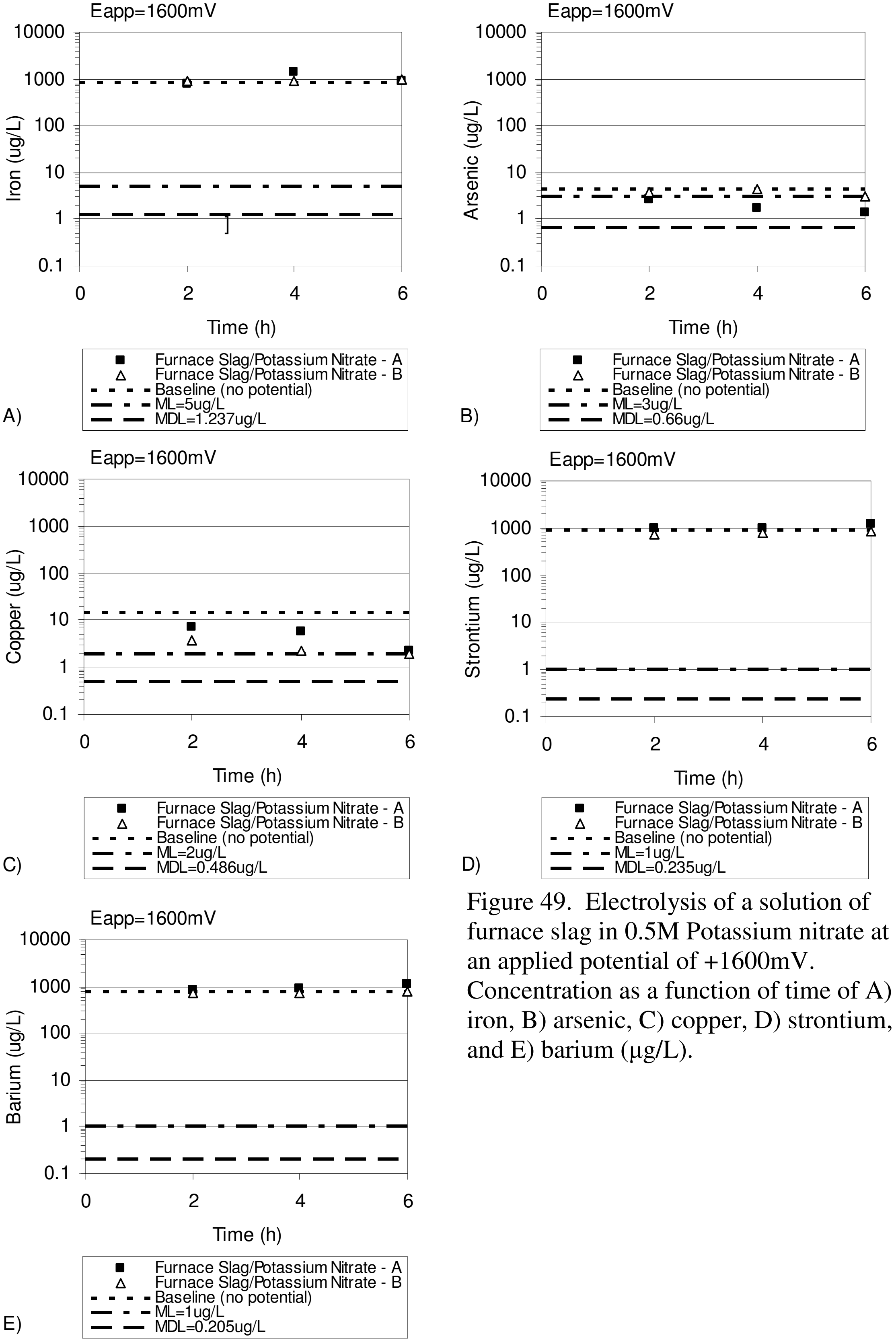


Figure 49. Electrolysis of a solution of furnace slag in 0.5M Potassium nitrate at an applied potential of +1600mV. Concentration as a function of time of A) iron, B) arsenic, C) copper, D) strontium, and E) barium (µg/L).

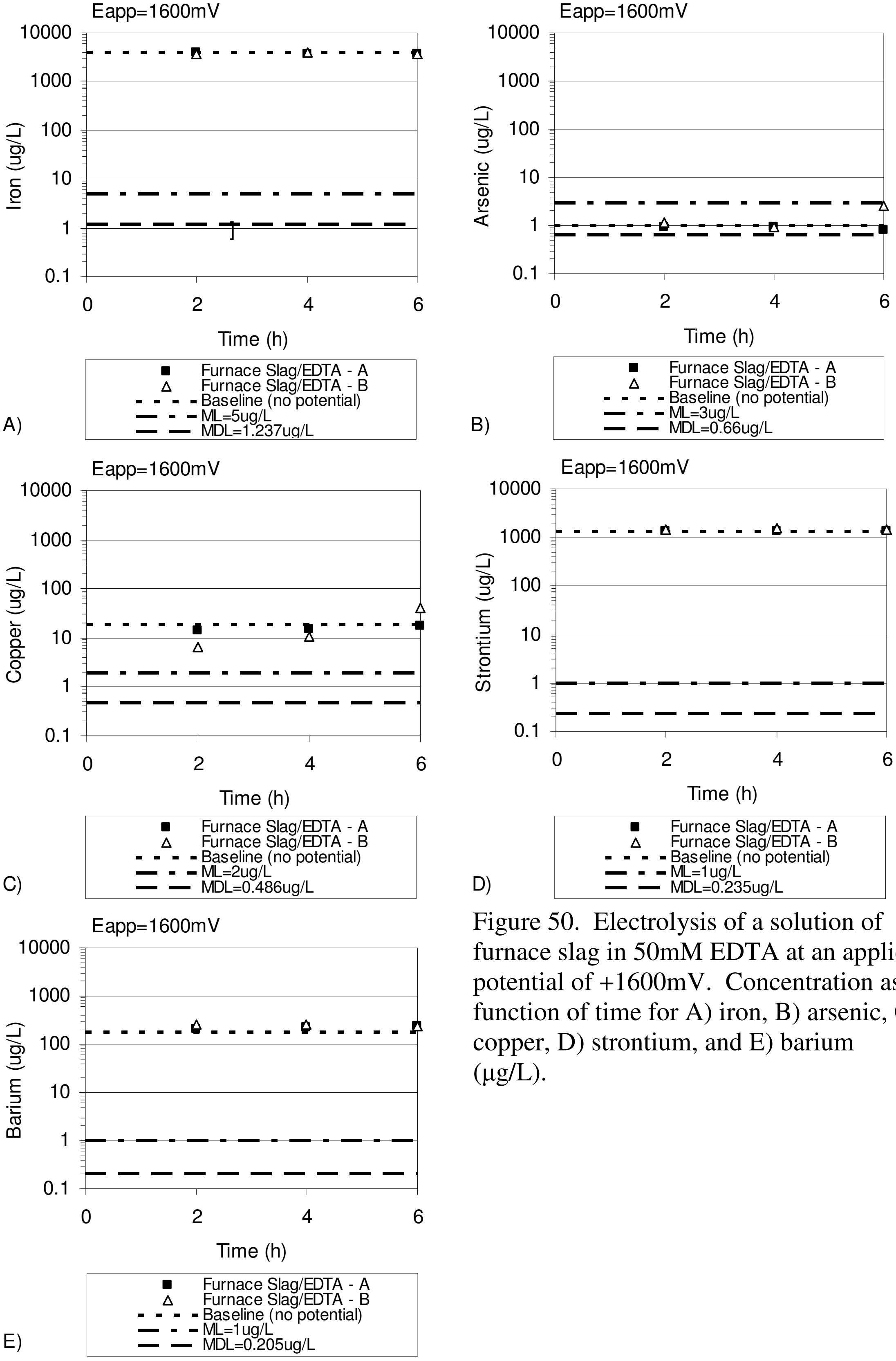


Figure 50. Electrolysis of a solution of furnace slag in 50mM EDTA at an applied potential of +1600mV. Concentration as a function of time for A) iron, B) arsenic, C) copper, D) strontium, and E) barium (μg/L).

Applied Potential of +2000mV (Figures 51-54)

At the applied potential of +2000mV, the current was negative and remained near a value of -20mA. This is in contrast with the baseline values of values of -99mA and -38mA for potassium nitrate and EDTA, respectively. The measured Eh and pH of the bulk solution did not change significantly over time for either cases. These results are presented in Figures 51 and 52 for potassium nitrate and EDTA, respectively. No significant change in iron, strontium, or barium concentration was observed independent of the electrolyte used. The arsenic data showed a slight increase from 4 to 14ug/L for the potassium nitrate, whereas with the EDTA, the values of arsenic in solution below the detection limits. The amount of copper in solution showed an overall decrease when potassium nitrate was used as an electrolyte, whereas no real trend was seen when EDTA was used. These results are presented in Figures 53 and 54.

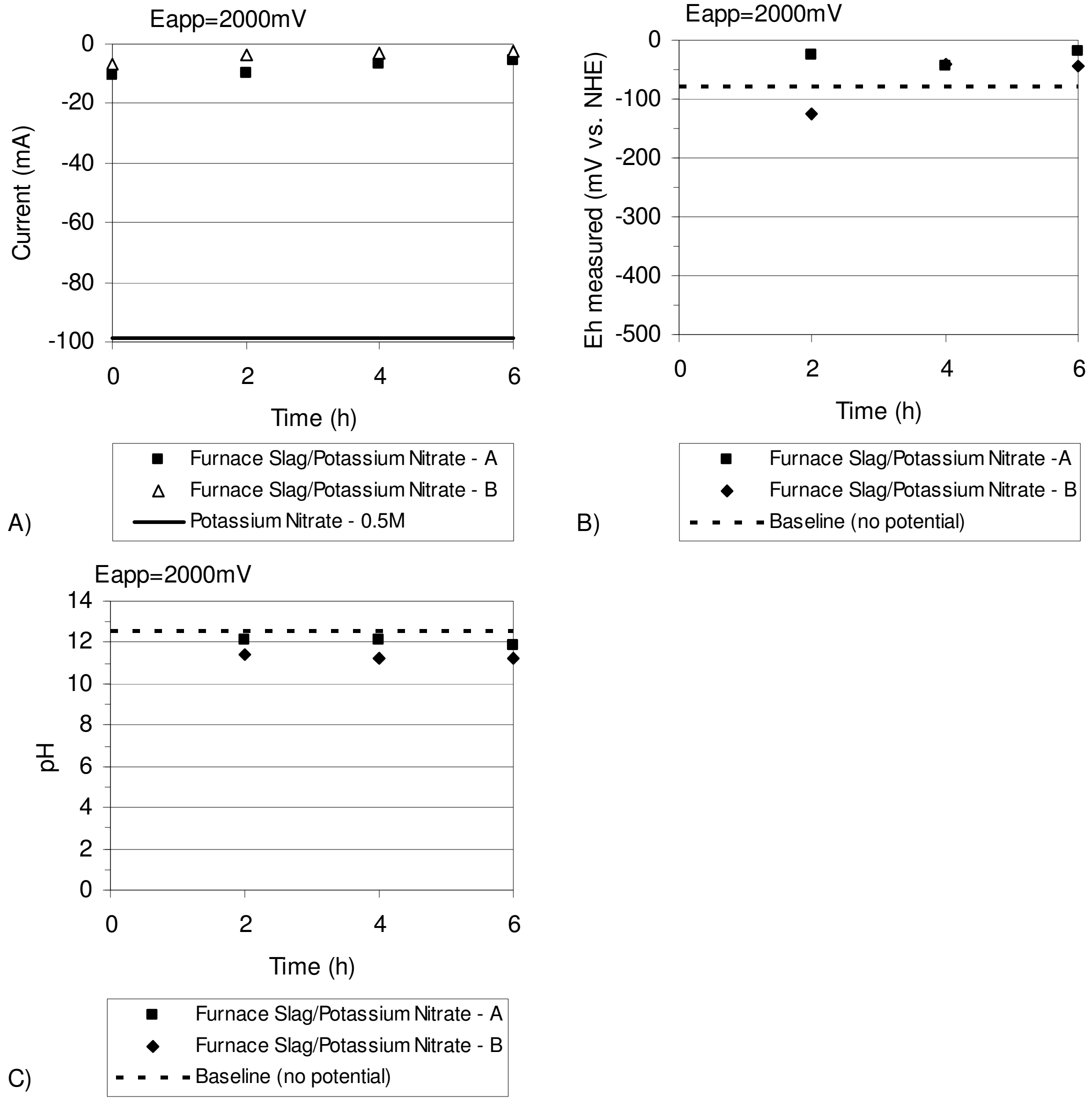


Figure 51. Electrolysis of a solution of furnace slag in 0.5M potassium nitrate at an applied potential of +2000mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.

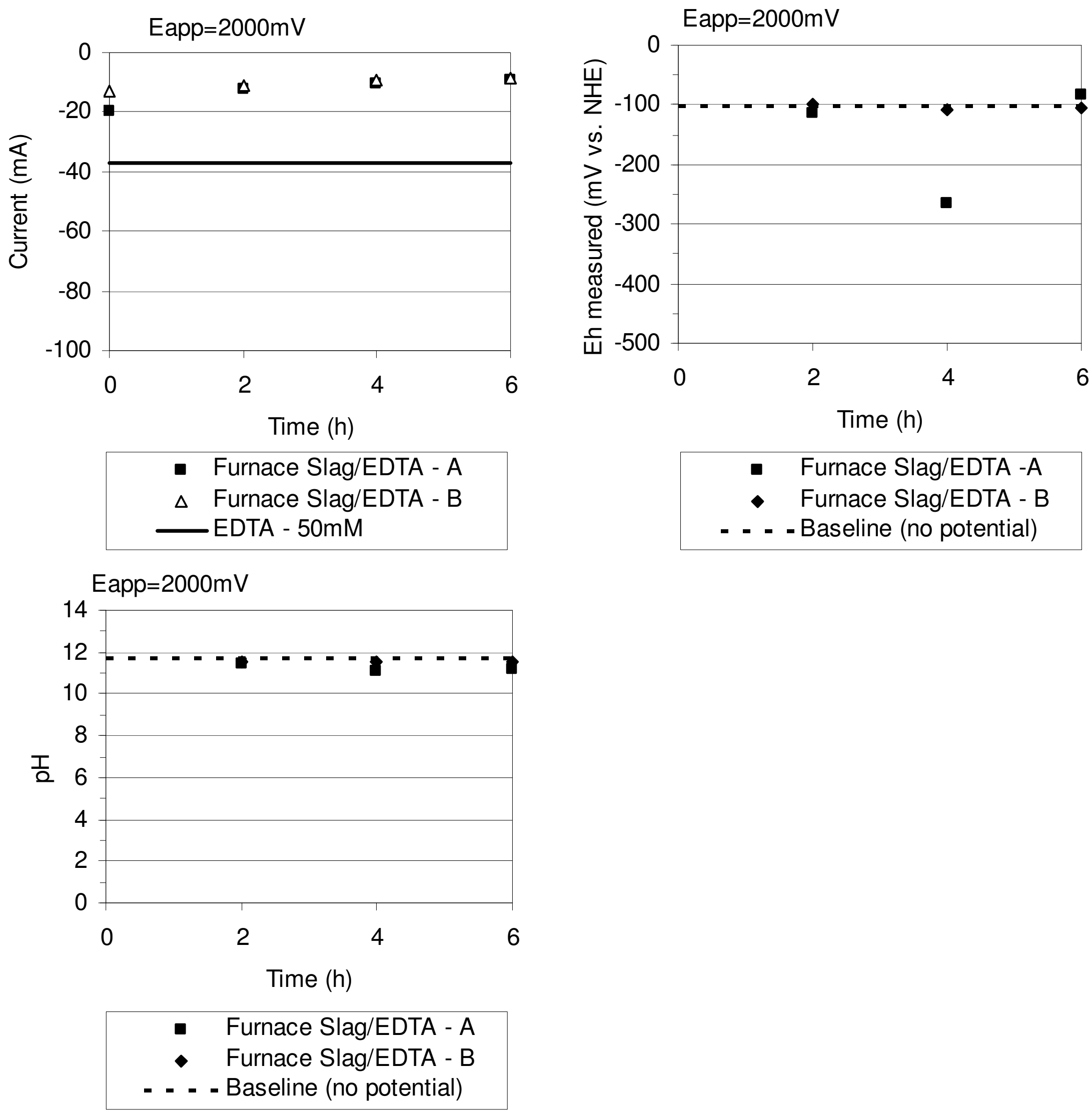
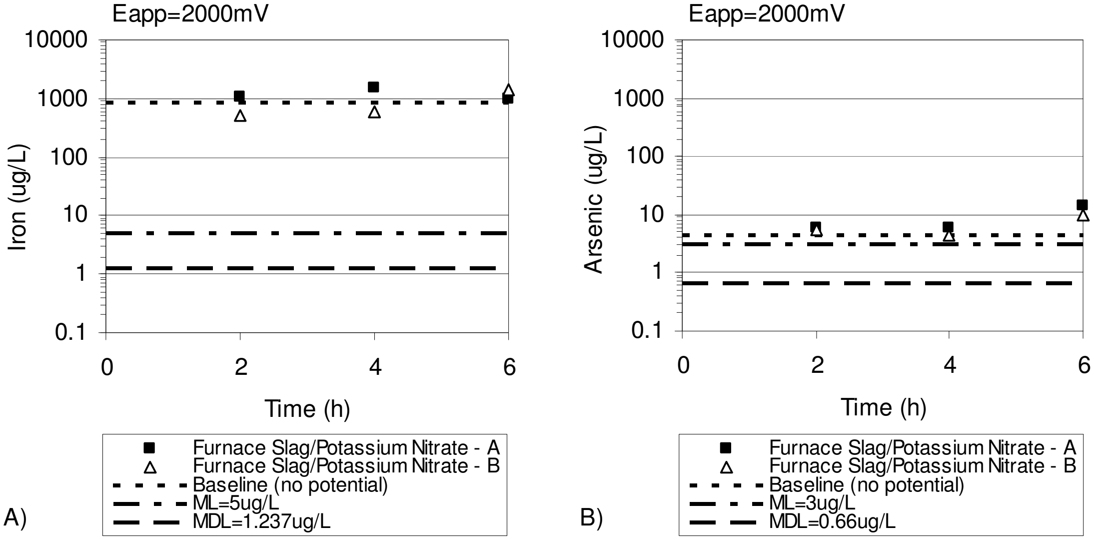
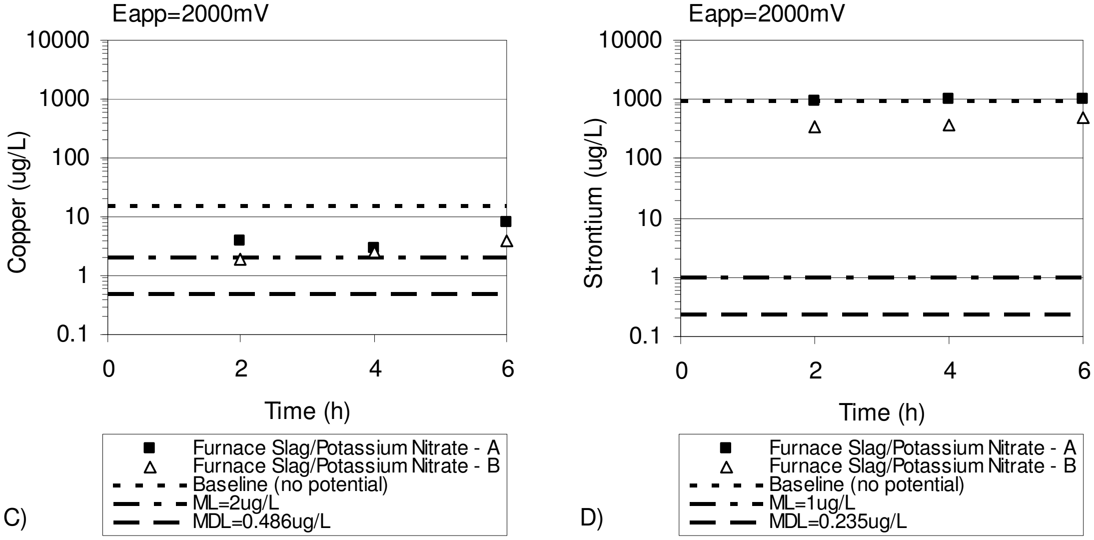


Figure 52. Electrolysis of a solution of furnace slag in 50mM EDTA at an applied potential of +2000mV. A) Faradic current as a function of time. B) Measured Eh as a function of time. C) Measured pH as a function of time.





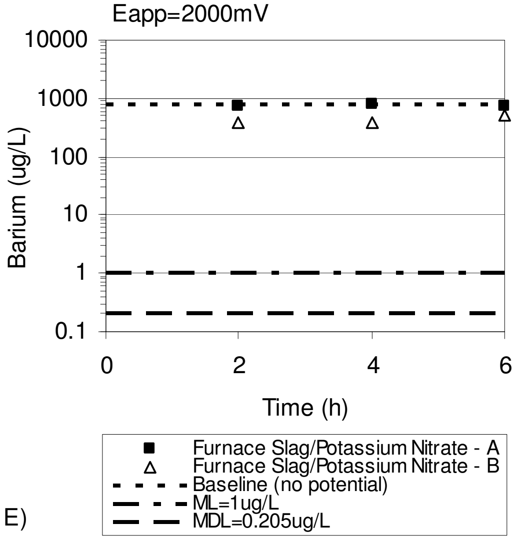


Figure 53. Electrolysis of a solution of furnace slag in 0.5M Potassium nitrate at an applied potential of +2000mV. Concentration as a function of time for A) iron, B) arsenic, C) copper, D) strontium, and E) barium (µg/L).

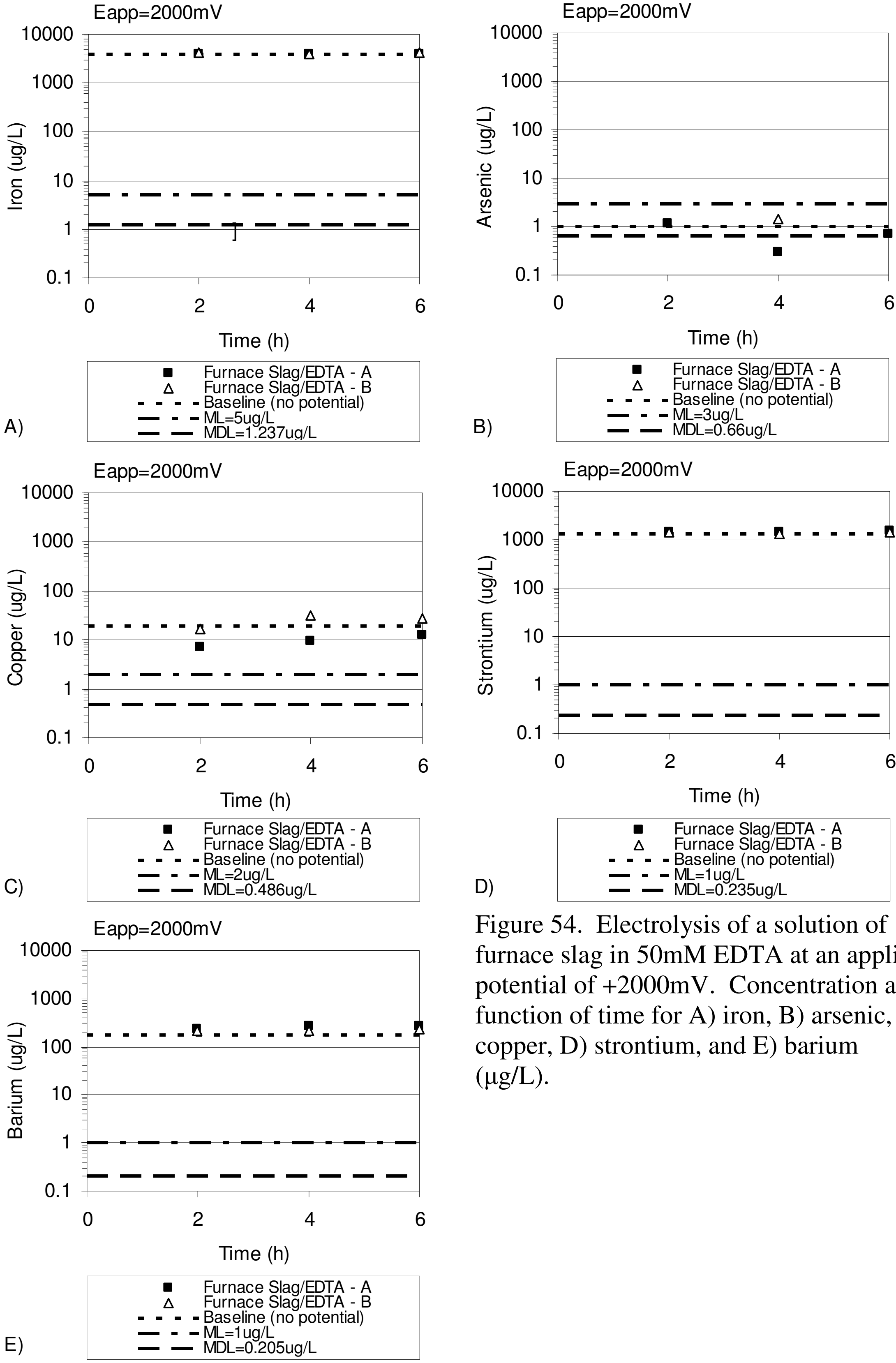


Figure 54. Electrolysis of a solution of furnace slag in 50mM EDTA at an applied potential of +2000mV. Concentration as a function of time for A) iron, B) arsenic, C) copper, D) strontium, and E) barium (µg/L).

Conclusions

The results showed that there was an effect of time on the current, measured bulk Eh, pH, and concentration data for both the iron(III) nitrate solution and the arsenic contaminated soil during the electrolysis experiments. The qualitative iron(II) results also suggested that the electrolytic system was capable of changing the oxidation state of the iron in solution. The electrolysis of the furnace slag had no noticeable effect (at the applied potentials tested: 0, +1600, and +2000mV) on the measured Eh, pH, or constituent concentration.

Effect of Varying Applied Potential

The effects of applied potentials after 6 hours of electrolysis on pH, Eh, and constituent concentration are presented in Figures 55 and 56 for the iron(III) nitrate solution and arsenic contaminated soil, respectively. Figure 57 shows a comparison of the electrolysis results with that of the solubility as a function of pH for iron, arsenic, and copper obtained using the SR002 procedure (SR002, "Alkalinity, Solubility and Release as a Function of pH" from the Integrated Framework for Evaluating Leaching (Kosson et al., 2002)).

For the iron(III) nitrate solution, as the applied potential was decreased, the pH increased, which was coupled with a decrease in the aqueous concentration of iron. This decrease in iron concentration was confirmed visually by the presence of a precipitate. These results suggest that the iron mobility and speciation of the iron(III) nitrate solution have been altered due to electrolysis. An Eh-pH diagram was also generated using Geochemist's Workbench (Rockware, Inc.; Golden, Co). This diagram shows that the

Eh-pH values where iron precipitated (high pH, low Eh) correspond to a solid form of iron. These results are presented in Figure 55.

For the arsenic contaminated soil suspensions, the pH steadily increased as the applied potential was decreased. The aqueous concentrations of both iron and copper also showed an increase as the applied potential decreased, while the aqueous concentration of arsenic did not appear to follow any noticeable trend. These results are presented in Figure 56.

For iron, the solubility seemed to be increased in comparison with the results of the SR002 between a pH of 6-8 (from less than 0.1mg/L to 1-10mg/L). At higher pH values (greater than 8), the redox did not affect the solubility. For arsenic, the solubility seemed to be increased in comparison with the results of the SR002 below a pH of around 10 (from 0.33mg/L to 4-6mg/L). Around the pH of 10, the arsenic solubility decreased in comparison with the results of the SR002 (from 24.8mg/L to around 2mg/L). These results suggested that the electrolysis of the soil suspension affected arsenic solubility. The results of the copper solubility are similar between the SR002 and electrolysis data, which suggested that there was little effect of redox on copper solubility.

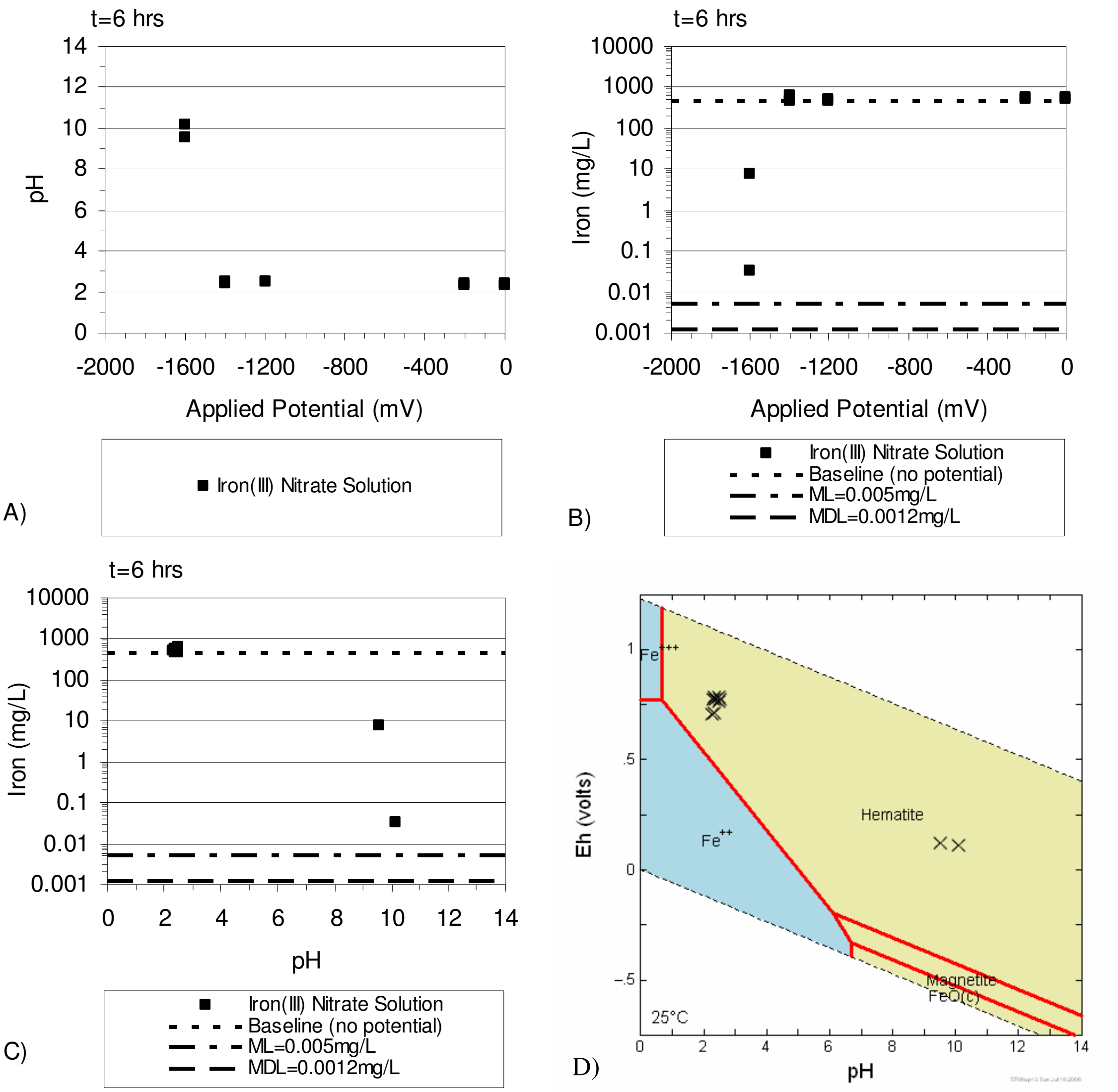


Figure 55. 0.01M iron(III) nitrate solutions after 6 hours of electrolysis for: A) pH as a function of applied potential, B) aqueous iron concentration as a function of applied potential, C) aqueous iron concentration as a function of pH, and D) iron Pourbaix diagram with overlaid data.

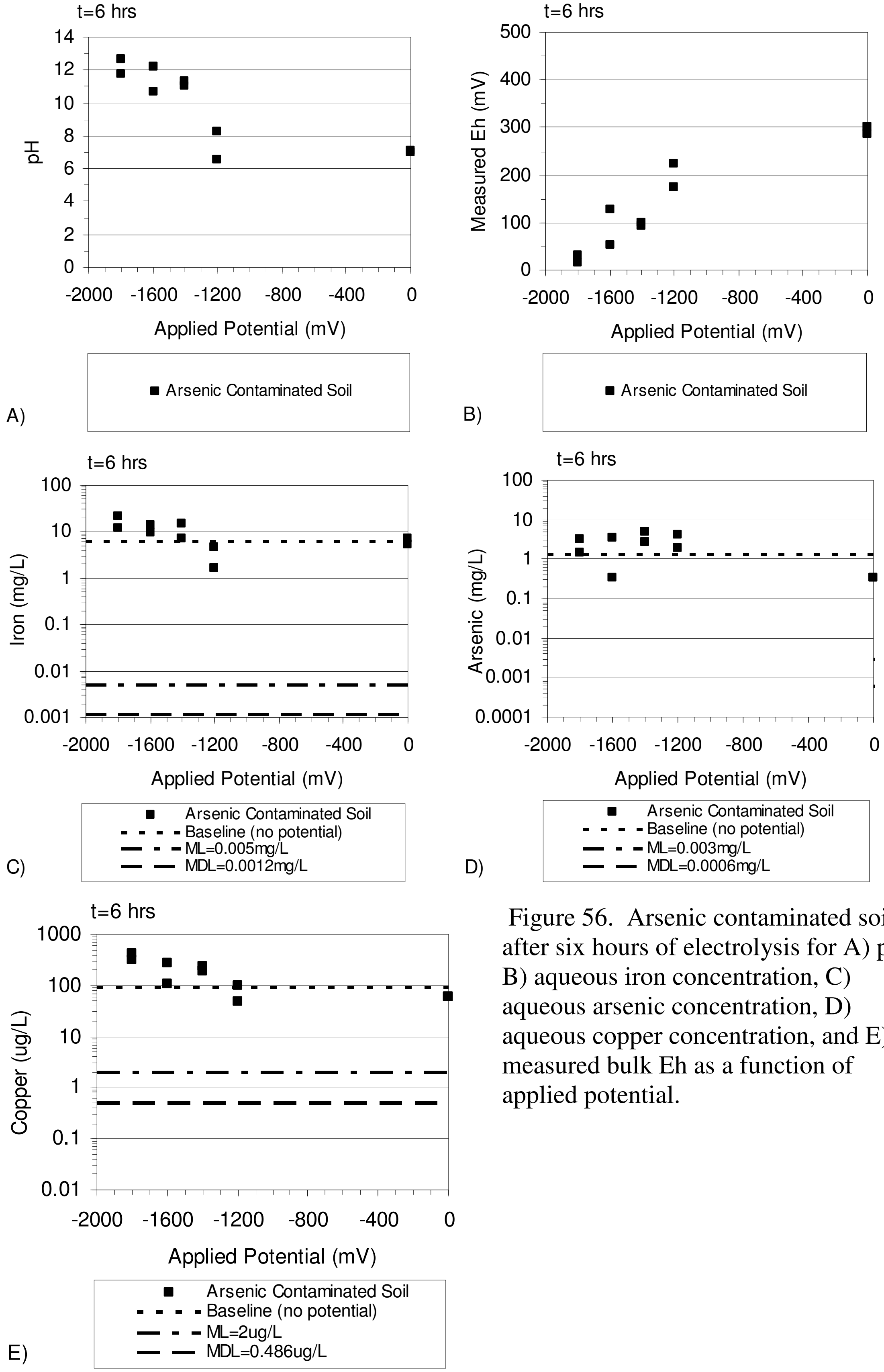


Figure 56. Arsenic contaminated soil after six hours of electrolysis for A) pH, B) aqueous iron concentration, C) aqueous arsenic concentration, D) aqueous copper concentration, and E) measured bulk Eh as a function of applied potential.

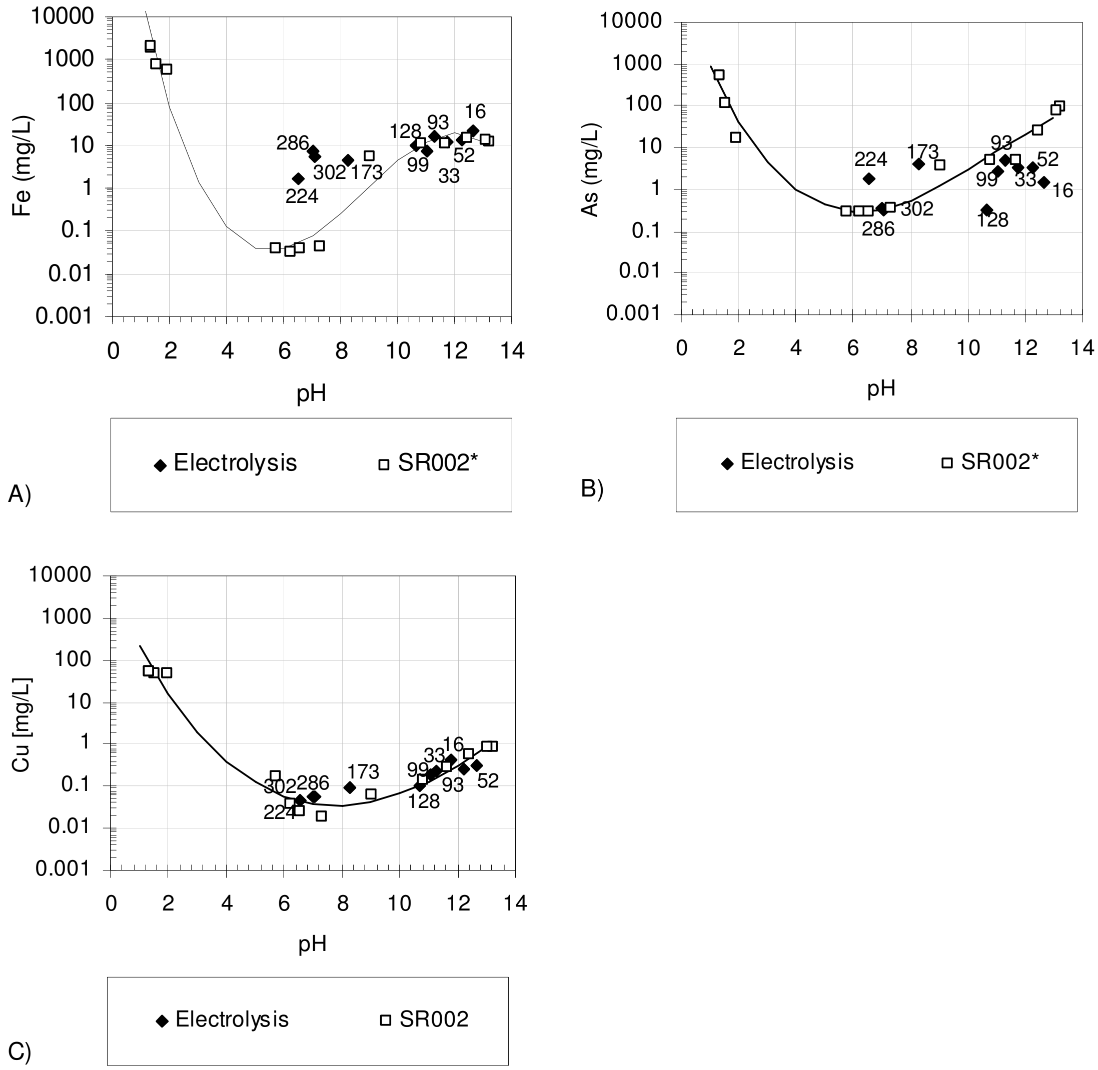


Figure 57. Comparison of electrolyte results (6 hours) with results of solubility as a function of pH obtained using the SR002 procedure. (Measured bulk Eh values from electrolysis are also given.)

Conclusions

The results suggested that varying applied potentials had an effect on the bulk measured Eh, pH, and aqueous concentration of constituents after a total of 6 hours. Generally, as the applied potential increased, the Eh of the bulk suspension decreased. The solubility of iron, arsenic, and copper from the electrolysis studies were compared to the results using procedure SR002. These results suggested that the solubility of arsenic and iron were altered as a function of Eh. In contrast, the solubility of copper was unaffected by the applied potentials.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Preliminary Studies

In the preliminary studies, iron(III) nitrate was determined to be a better iron source than iron oxide due to its high solubility and good reproducibility. Iron(II) nitrate was then chosen to be the test system in the second set of studies. The copper pipe and carbon rod seemed to perform similarly; however, the carbon rod was ultimately chosen due to its inertness. No effect was seen based on the type of salt (potassium nitrate or sodium chloride) used in the salt bridge. Since nitrate ions would already be present in the test solution, potassium nitrate was chosen as the electrolyte in both the salt bridge and solution.

Electrolytic Oxidation/Reduction Studies

Effect of Time during the Electrolysis

Iron Nitrate Solutions

The electrolysis of 0.01M iron(III) nitrate was shown to have an effect on current, bulk solution Eh, pH, and aqueous iron concentrations as a function of time. Even at

0mV of applied potential where no changes were seen in the bulk solution Eh and pH, the concentration of iron(II) in solution increased from less than 0.5mg/L to 3-4mg/L (qualitative results). However, no significant changes were seen in the total concentration of iron in solution. Slight changes (50-100mV) were seen in the measured bulk Eh at applied potentials of -200, -1200, and -1400mV; however, no significant change in pH and iron concentration were observed. In contrast, significant changes in bulk solution Eh, pH, and aqueous iron concentration were seen at an applied potential of -1600mV. The bulk solution Eh decreased from 825mV to about 100mV, and the pH increased from around 2.3 to around 10. This significant change in Eh and pH was coupled to iron precipitation. The decrease in aqueous iron concentration from around 480mg/L to less than 10mg/L, as well as the data from the qualitative iron(II) test, suggested that iron did indeed precipitate out of solution. The results at an applied potential of -1800mV also showed a similar precipitation event, but the significant changes in measured bulk Eh and pH were not obtained. This may be due to the fact that the current was significantly below the baseline value. Also, -1800mV was only applied for a total of 1.5 hours, which may have needed to have been longer in order to observe the full effect of the electrolysis. Overall, these results suggest that the electrolytic technique was capable of affecting the measured bulk Eh, pH, and oxidation state of iron(III) nitrate in solution.

Arsenic Contaminated Soil

Overall, for the applied potentials of -1200, -1400, -1600, and -1800mV, the electrolytic technique was shown to be capable of causing significant changes in the bulk solution Eh (from 323mV to as low as 16mV). This was accompanied with a significant change in the solution pH (from 6.6 to as high as 12.7). Increases in the amount of iron, arsenic and copper were seen at -1400 and -1800mV. For -1200 and -1600mV, no significant trend in the aqueous concentrations was noted. Further replicated may be needed in order to better understand the trends of the aqueous concentrations of the constituents in the arsenic contaminated soil suspension. Using a chelating agent, EDTA, for 24-48 hours prior to electrolysis could also make more of the constituents available for reduction.

Furnace Slag

No significant changes were noted in the measured Eh, pH, or aqueous constituent concentrations when the furnace slag was subjected to the electrolytic technique. The electrolytic technique, as currently designed, does not appear to be capable of oxidizing a reduced system. Changing the working electrode to a different material capable of applying higher potentials (+2000mV or greater) is one suggestion to address this problem. Also, the furnace slag in 0.05M EDTA may have not been conductive enough to allow for oxidation to occur. Adding 0.5M potassium nitrate in addition to the 0.5M EDTA at varying applied potentials would be another step in determining if the electrolytic technique can be used in order to oxidize a system.

Effect of Varying Applied Potentials

Varying applied potential had an effect on the measured bulk Eh, pH, and aqueous concentration of constituents after a total of 6 hours of electrolysis. As the applied potential increased for both the iron(III) nitrate solution and the arsenic contaminated soil suspension, the Eh decreased; however, this was accompanied by a pH increase. These results agree with what is expected, since Eh and pH are coupled processes. The solubility of iron, arsenic, and copper from the electrolysis studies were compared to the results using the SR002 procedure. In contrast, the solubility of copper was unaffected by the applied potentials.

Recommendations

Due to time constraints, the effect of keeping the counter electrode and salt bridge separate from the electrolytic cell was not tested. This could be done by placing the counter electrode in a separate small container filled with an appropriate electrolyte solution placed outside of the electrolytic cell. The purpose of this study would be to ensure that the counter reactions occurring at the counter electrode were not reoxidizing the constituents previously reduced by the working electrode.

For the arsenic contaminated soil and furnace slag, the electrolytic technique should be tested using as the electrolyte a solution of 0.5M potassium nitrate and 0.05M EDTA in order to increase the amount of constituents into solution that would be available for electrolysis. The additional constituents in solution may allow for greater changes in the bulk solution Eh and aqueous constituent concentrations.

The final recommendation would be to allow for greater times of electrolysis (greater than 6 hours) in order to see the effect that greater periods of time have on the bulk solution Eh, pH, and the concentrations of the constituents.

APPENDIX A

PRELIMINARY RESULTS

0.006M Fe as Iron Nitrate NaCl salt bridge
Carbon rod working electrode Replicate #1

Eapplied (V)	Current (mA)	Current t=1min	Eh (mV)	Eh v. NHE (mV)	pH
0			587.1	784.1	2.141
0	0.003	0.001	584.3	781.3	2.147
-0.1	0.008	0.001	582.3	779.3	2.151
-0.2	0.005	0.001	580.5	777.5	2.154
-0.3	0.003	0.001	577.4	774.4	2.16
-0.4	0.011	0.003	574.8	771.8	2.167
-0.5	0.015	0.003	571.5	768.5	2.176
-0.6	0.025	0.004	569	766	2.184
-0.7	0.009	0.004	567.4	764.4	2.189
-0.8	0.018	0.005	565.6	762.6	2.194
-0.9	0.032	0.008	564.4	761.4	2.199
-1	0.089	0.011	561.6	758.6	2.211
-1.1	0.081	0.017	560.4	757.4	2.22
-1.2	0.084	0.018	559.2	756.2	2.234
-1.3	0.107	0.023	558.3	755.3	2.244
-1.4	0.114	0.051	557.4	754.4	2.264
-1.5	0.141	0.08	556.2	753.2	2.297
-1.6	0.211	0.131	554.4	751.4	2.338
-1.7	0.291	0.246	547.1	744.1	2.478
-1.8	0.44	0.341	539.2	736.2	2.591
-1.9	0.501	0.427	523	720	2.729
-2	0.651	0.549	469	666	2.985
-1.9	0.529	0.477	-167.5	29.5	10.508
-1.8	1.064	0.374	-175	22	10.998
-1.7	0.424	0.287	-171.5	25.5	11.173
-1.6	0.35	0.215	-170.1	26.9	11.299
-1.5	0.263	0.151	-137.3	59.7	11.613
-1.4	0.192	0.108	-130.8	66.2	11.618
-1.3	0.12	0.072	-126.3	70.7	11.62
-1.2	0.08	0.04	-124.4	72.6	11.618
-1.1	0.04	0.015	-121.2	75.8	11.616
-1	0.195	0.007	-119.3	77.7	11.612
-0.9	0.013	0.004	-115.4	81.6	11.606
-0.8	0.025	0.003	-110.1	86.9	11.596
-0.7	0.01	0.003	-105.4	91.6	11.606
-0.6	0.001	0.001	-106.6	90.4	11.588
-0.5	-0.001	0	-105.2	91.8	11.586
-0.4	-0.003	-0.001	-103.8	93.2	11.583
-0.3	0	-0.003	-102.4	94.6	11.579
-0.2	-0.009	-0.003	-100.9	96.1	11.575
-0.1	-0.185	-0.004	-99.3	97.7	11.573
0	-0.003	-0.003	-96.7	100.3	11.568

0.0006M Fe as Iron Nitrate	NaCl salt bridge
Carbon rod working electrode	Replicate #2

Eapplied (V)	Current (mA)	Current t=1min	Eh (mV)	Eh v. NHE (mV)	pH
0			593.9	790.9	2.391
0	0.019	0.002	591	788	2.392
-0.1	0.009	0.003	586.1	783.1	2.396
-0.2	0.009	0.003	584	781	2.398
-0.3	0.009	0.003	581	778	2.401
-0.4	0.017	0.004	578.3	775.3	2.404
-0.5	0.017	0.006	576.3	773.3	2.406
-0.6	0.029	0.007	573.9	770.9	2.409
-0.7	0.029	0.007	571.3	768.3	2.413
-0.8	0.024	0.008	568.5	765.5	2.418
-0.9	0.035	0.008	565.7	762.7	2.421
-1	0.046	0.011	564.3	761.3	2.424
-1.1	0.04	0.017	563.1	760.1	2.425
-1.2	0.056	0.021	562.3	759.3	2.427
-1.3	0.076	0.025	561.7	758.7	2.431
-1.4	0.152	0.046	561	758	2.443
-1.5	0.123	0.079	560.1	757.1	2.459
-1.6	0.147	0.108	559	756	2.476
-1.7	0.319	0.167	556.3	753.3	2.519
-1.8	0.385	0.251	551.7	748.7	2.577
-1.9	0.363	0.327	544.4	741.4	2.635
-2	0.463	0.428	514.6	711.6	2.82
-1.9	0.413	0.411	-176	21	11.079
-1.8	0.381	0.343	-179	18	11.276
-1.7	0.331	0.271	-179.3	17.7	11.314
-1.6	0.383	0.201	-178.2	18.8	11.337
-1.5	0.242	0.132	-176.1	20.9	11.34
-1.4	0.169	0.097	-175.3	21.7	11.349
-1.3	0.108	0.069	-173.2	23.8	11.355
-1.2	0.077	0.043	-170.3	26.7	11.351
-1.1	0.032	0.021	-167.7	29.3	11.347
-1	0.081	0.07	-160	37	11.325
-0.9	0.011	0.003	-154.4	42.6	11.308
-0.8	0.005	0.001	-150.7	46.3	11.296
-0.7	0	0.001	-148.4	48.6	11.288
-0.6	-0.005	0	-145.6	51.4	11.28
-0.5	-0.015	0	-141.4	55.6	11.269
-0.4	-0.004	-0.001	-137.3	59.7	11.255
-0.3	-0.005	-0.001	-133	64	11.241
-0.2	-0.008	-0.003	-132	65	11.238
-0.1	-0.01	-0.004	-130.7	66.3	11.235
0	-0.013	-0.004	-128.3	68.7	11.227

0.01M Fe as Iron Oxide NaCl salt bridge
Carbon rod working electrode Replicate #1

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			100	297	7.43
0	-0.001	-0.001	110.6	307.6	7.23
-0.1	0.001	-0.001	116.4	313.4	7.093
-0.2	0.003	0.001	118.2	315.2	7.092
-0.3	0.027	0.003	114.1	311.1	7.543
-0.4	0.061	0.003	98.5	295.5	8.619
-0.5	0.303	0.004	95.9	292.9	8.952
-0.6	0.028	0.005	95.1	292.1	9.158
-0.7	0.025	0.005	94.9	291.9	9.326
-0.8	0.056	0.006	95.1	292.1	9.452
-0.9	0.085	0.007	95.5	292.5	9.574
-1	0.095	0.007	97.6	294.6	9.667
-1.1	0.08	0.008	94.3	291.3	9.773
-1.2	0.04	0.014	64.8	261.8	9.864
-1.3	0.265	0.032	-8.5	188.5	10.092
-1.4	0.209	0.084	-52.3	144.7	10.54
-1.5	0.236	0.163	-82.9	114.1	10.925
-1.6	0.635	0.268	-97.6	99.4	11.094
-1.7	0.407	0.359	-119.6	77.4	11.36
-1.8	0.591	0.483	-137.3	59.7	11.529
-1.9	0.627	0.605	-147.3	49.7	11.623
-2	0.749	0.754	-151.4	45.6	11.72
-1.9	0.667	0.619	-160.3	36.7	11.772
-1.8	0.497	0.49	-159.3	37.7	11.79
-1.7	0.384	0.37	-151.4	45.6	11.806
-1.6	0.28	0.26	-45	152	11.808
-1.5	0.179	0.157	-140.6	56.4	11.796
-1.4	0.104	0.079	-131.6	65.4	11.792
-1.3	0.057	0.032	-124.3	72.7	11.784
-1.2	0.025	0.012	-114	83	11.775
-1.1	0.045	0.005	-102.7	94.3	11.768
-1	0.011	0.005	-97	100	11.764
-0.9	0.01	0.004	-84	113	11.758
-0.8	0.114	0.003	-77	120	11.755
-0.7	0.008	0.002	-69	128	11.751
-0.6	0.005	0.001	-60	137	11.748
-0.5	-0.001	0	-50	147	11.745
-0.4	-0.002	0	-30.2	166.8	11.742
-0.3	-0.003	-0.001	10	207	11.736
-0.2	-0.005	-0.002	30.2	227.2	11.73
-0.1	-0.01	-0.001	60.8	257.8	11.725
0	-0.031	-0.002	132	329	11.708

0.01M Fe as Iron Oxide NaCl salt bridge
Carbon rod working electrode Replicate #2

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			158	355	5.946
0	-0.004	-0.001	156.3	353.3	5.967
-0.1	-0.001	-0.001	155.5	352.5	5.979
-0.2	0.001	0	155	352	6.012
-0.3	0.002	0.001	154.6	351.6	6.077
-0.4	0.009	0.002	152.8	349.8	6.274
-0.5	0.042	0.003	148.3	345.3	6.566
-0.6	0.02	0.004	134.3	331.3	7.588
-0.7	0.019	0.005	116.1	313.1	8.626
-0.8	0.037	0.005	105.6	302.6	9.171
-0.9	0.037	0.006	102.7	299.7	9.362
-1	0.034	0.006	100.1	297.1	9.527
-1.1	0.046	0.01	94.8	291.8	9.709
-1.2	0.032	0.037	23	220	10.037
-1.3	0.106	0.075	-18.6	178.4	10.274
-1.4	0.161	0.056	-44.9	152.1	10.478
-1.5	0.142	0.061	-65	132	10.709
-1.6	0.116	0.097	-63.3	133.7	10.849
-1.7	0.173	0.143	-84.3	112.7	11.064
-1.8	0.232	0.2	-93.4	103.6	11.198
-1.9	0.27	0.248	-99.3	97.7	11.273
-2	0.314	0.31	-109.3	87.7	11.355
-1.9	0.36	0.262	-113.3	83.7	11.411
-1.8	0.221	0.21	-112.6	84.4	11.446
-1.7	0.195	0.16	-108.9	88.1	11.47
-1.6	0.143	0.117	-101.5	95.5	11.479
-1.5	0.134	0.09	-90	107	11.496
-1.4	0.035	0.018	-82.4	114.6	11.495
-1.3	0.016	0.008	-74.6	122.4	11.494
-1.2	0.015	0.005	-66.3	130.7	11.491
-1.1	0.008	0.002	-52.1	144.9	11.485
-1	0.01	0.002	-40.4	156.6	11.482
-0.9	0.013	0.002	-32.3	164.7	11.479
-0.8	0.006	0.002	-27	170	11.476
-0.7	0.005	0.002	-17	180	11.473
-0.6	0.001	0.001	-7.5	189.5	11.47
-0.5	0	0	25.4	222.4	11.468
-0.4	0	0	66.7	263.7	11.46
-0.3	0.002	-0.001	92.1	289.1	11.459
-0.2	-0.005	-0.002	111.8	308.8	11.455
-0.1	-0.006	-0.002	195.7	392.7	11.431
0	-0.008	-0.002	207.3	404.3	11.425

0.01M Fe in Iron Nitrate KNO3 salt bridge
Carbon rod working electrode Replicate #1

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			602.1	799.1	2.693
0	-0.066	0.001	580.8	777.8	2.667
-0.1	0.006	0.002	576.6	773.6	2.665
-0.2	0.009	0.002	571.2	768.2	2.66
-0.3	0.008	0.003	568.3	765.3	2.658
-0.4	0.008	0.004	563.2	760.2	2.654
-0.5	0.013	0.005	560.5	757.5	2.653
-0.6	0.015	0.006	551.6	748.6	2.623
-0.7	0.032	0.007	548.8	745.8	2.622
-0.8	0.033	0.007	547	744	2.622
-0.9	0.042	0.008	545.6	742.6	2.622
-1	0.062	0.01	543.2	740.2	2.625
-1.1	0.056	0.017	541.2	738.2	2.634
-1.2	0.133	0.017	540.2	737.2	2.641
-1.3	0.072	0.026	538.9	735.9	2.655
-1.4	0.094	0.054	536.4	733.4	2.682
-1.5	0.138	0.089	532.8	729.8	2.709
-1.6	0.182	0.123	524.1	721.1	2.756
-1.7	0.298	0.18	500.1	697.1	2.847
-1.8	0.368	0.242	432.3	629.3	3.056
-1.9	0.37	0.317	-102.5	94.5	8.931
-2	0.475	0.394	-134.9	62.1	11.027
-1.9	0.483	0.344	-144.1	52.9	11.301
-1.8	0.361	0.298	-145.7	51.3	11.399
-1.7	0.337	0.248	-143.4	53.6	11.444
-1.6	0.269	0.201	-137	60	11.496
-1.5	0.221	0.17	-129.5	67.5	11.518
-1.4	0.17	0.127	-123.2	73.8	11.523
-1.3	0.105	0.085	-109.4	87.6	11.525
-1.2	0.089	0.053	-104	93	11.514
-1.1	0.032	0.022	-98.2	98.8	11.503
-1	0.014	0.008	-92.4	104.6	11.489
-0.9	0.011	0.003	-87.7	109.3	11.475
-0.8	0.006	0.003	-80.1	116.9	11.453
-0.7	0.008	0.002	-76	121	11.442
-0.6	0.013	0.002	-72.9	124.1	11.431
-0.5	0.007	0.001	-69.1	127.9	11.42
-0.4	0.006	0.001	-66.5	130.5	11.412
-0.3	-0.001	-0.001	-62	135	11.4
-0.2	-0.005	-0.002	-58.6	138.4	11.391
-0.1	-0.006	-0.002	-56.4	140.6	11.385
0	-0.027	-0.002	-52.1	144.9	11.369

0.06M Fe as Iron Nitrate KNO3 salt bridge
Carbon rod working electrode Replicate #2

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			601.5	798.5	2.29
0	0.004	0.001	590.4	787.4	2.374
-0.1	0.003	0.001	582.6	779.6	2.383
-0.2	0.003	0.001	579	776	2.383
-0.3	0.01	0.001	575.8	772.8	2.38
-0.4	0.005	0.002	571	768	2.375
-0.5	0.006	0.002	568	765	2.371
-0.6	0.012	0.003	564.7	761.7	2.368
-0.7	0.011	0.004	562.8	759.8	2.368
-0.8	0.019	0.005	561.4	758.4	2.365
-0.9	0.015	0.005	559.9	756.9	2.364
-1	0.055	0.007	558.2	755.2	2.364
-1.1	0.042	0.01	556.4	753.4	2.37
-1.2	0.056	0.014	555.8	752.8	2.373
-1.3	0.042	0.017	555.2	752.2	2.381
-1.4	0.123	0.034	553.5	750.5	2.421
-1.5	0.064	0.049	552.8	749.8	2.435
-1.6	0.111	0.072	548.6	745.6	2.515
-1.7	0.131	0.104	538.1	735.1	2.632
-1.8	0.196	0.134	515.8	712.8	2.787
-1.9	0.21	0.169	478.1	675.1	3
-2	0.27	0.198	-106	91	9.467
-1.9	0.246	0.181	-108.6	88.4	10.389
-1.8	0.194	0.154	-106.4	90.6	10.743
-1.7	0.169	0.138	-100.1	96.9	10.907
-1.6	0.141	0.117	-94.1	102.9	11.009
-1.5	0.111	0.094	-89	108	11.07
-1.4	0.088	0.07	-84.7	112.3	11.088
-1.3	0.12	0.049	-81	116	11.09
-1.2	0.039	0.03	-72	125	11.083
-1.1	-0.001	0.015	-70.6	126.4	11.082
-1	-0.001	0.006	-68.1	128.9	11.068
-0.9	0.005	0.002	-65.7	131.3	11.053
-0.8	0.004	0.001	-64.1	132.9	11.045
-0.7	0.024	0.001	-59.7	137.3	11.022
-0.6	0.001	0.001	-56.6	140.4	11.006
-0.5	0.001	0.001	-55.2	141.8	10.998
-0.4	-0.002	0	-53.3	143.7	10.988
-0.3	-0.007	-0.002	-51.7	145.3	10.977
-0.2	-0.003	-0.002	-50.2	146.8	10.969
-0.1	-0.001	-0.003	-49	148	10.962
0	-0.006	-0.002	-44	153	10.936

0.006M Fe as Iron Nitrate NaCl salt bridge
Copper pipe working electrode Replicate #1

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			565.3	762.3	2.641
0	-0.063	-0.085	523	720	2.739
-0.1	-0.014	-0.013	513.4	710.4	2.776
-0.2	0.059	0.001	510.7	707.7	2.777
-0.3	0.007	0.003	509.8	706.8	2.779
-0.4	0.134	0.005	509.3	706.3	2.78
-0.5	0.011	0.006	508.9	705.9	2.781
-0.6	0.057	0.006	508.3	705.3	2.783
-0.7	0.026	0.006	507.7	704.7	2.783
-0.8	0.066	0.01	506.7	703.7	2.786
-0.9	0.031	0.014	506.3	703.3	2.788
-1	0.101	0.018	505.4	702.4	2.79
-1.1	0.058	0.026	504.8	701.8	2.794
-1.2	0.2	0.036	503.6	700.6	2.799
-1.3	0.259	0.049	502.7	699.7	2.803
-1.4	0.148	0.054	500.4	697.4	2.811
-1.5	0.138	0.061	495.8	692.8	2.811
-1.6	21	0.118	485.1	682.1	2.85
-1.7	0.241	0.216	437.6	634.6	2.982
-1.8	0.245	0.316	200.1	397.1	5.013
-1.9	0.424	0.443	-90.5	106.5	10.748
-2	0.568	0.619	-107.3	89.7	11.394
-1.9	0.872	0.522	-97.7	99.3	11.552
-1.8	0.456	0.416	-92.8	104.2	11.649
-1.7	0.349	0.309	-92.3	104.7	11.668
-1.6	0.307	0.214	-92	105	11.687
-1.5	0.28	0.137	-86	111	11.694
-1.4	0.478	0.133	-81.6	115.4	11.697
-1.3	0.242	0.072	-77.7	119.3	11.697
-1.2	0.082	0.046	-72.3	124.7	11.695
-1.1	0.036	0.017	-65.1	131.9	11.685
-1	0.022	0.008	-61.4	135.6	11.68
-0.9	0.018	0.006	-58.3	138.7	11.675
-0.8	0.016	0.005	-51.4	145.6	11.665
-0.7	0.014	0.004	-45	152	11.657
-0.6	0.016	0.003	-40.1	156.9	11.651
-0.5	0.006	0.002	-33.6	163.4	11.644
-0.4	0.002	0.002	-30.3	166.7	11.634
-0.3	-0.003	-0.002	-25.1	171.9	11.636
-0.2	0.001	0.001	-19.3	177.7	11.632
-0.1	-0.01	-0.001	-12	185	11.627
0	-0.004	-0.002	6.6	203.6	11.614

0.06M Fe as Iron Nitrate NaCl salt bridge
Copper pipe working electrode Replicate #2

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			558.3	755.3	2.468
0	-0.09	-0.09	540.3	737.3	2.515
-0.1	-0.078	-0.083	530.2	727.2	2.549
-0.2	0.003	0.002	526.8	723.8	2.572
-0.3	0.01	0.004	521.3	718.3	2.593
-0.4	0.008	0.005	519.7	716.7	2.592
-0.5	0.014	0.007	518.5	715.5	2.59
-0.6	0.023	0.008	517.3	714.3	2.59
-0.7	0.024	0.01	516.2	713.2	2.592
-0.8	0.022	0.014	514.6	711.6	2.596
-0.9	0.041	0.02	511.1	708.1	2.616
-1	0.072	0.026	510.2	707.2	2.626
-1.1	0.135	0.032	508.9	705.9	2.643
-1.2	0.111	0.053	508	705	2.651
-1.3	0.123	0.07	506.7	703.7	2.666
-1.4	0.183	0.082	502.7	699.7	2.706
-1.5	0.256	0.096	497.2	694.2	2.75
-1.6	0.22	0.138	483	680	2.804
-1.7	0.331	0.25	385.2	582.2	3.003
-1.8	0.368	0.362	177.7	374.7	4.761
-1.9	0.521	0.495	-229.1	-32.1	10.999
-2	0.704	0.746	-264.7	-67.7	11.319
-1.9	0.672	0.658	-266.3	-69.3	11.409
-1.8	0.53	0.51	-264.8	-67.8	11.466
-1.7	0.485	0.379	-265.4	-68.4	11.553
-1.6	0.333	0.271	-255.6	-58.6	11.571
-1.5	0.269	0.177	-238.2	-41.2	11.579
-1.4	0.213	0.118	-198	-1	11.586
-1.3	0.218	0.098	-190.3	6.7	11.579
-1.2	0.106	0.065	-181.2	15.8	11.574
-1.1	0.148	0.03	-161.5	35.5	11.581
-1	0.055	0.013	-155	42	11.575
-0.9	0.019	0.006	-138.1	58.9	11.566
-0.8	0.026	0.004	-127.3	69.7	11.558
-0.7	0.023	0.004	-98.5	98.5	11.531
-0.6	0.019	0.003	-96.2	100.8	11.529
-0.5	0.007	0.002	-90.3	106.7	11.522
-0.4	0.005	0.002	-87.2	109.8	11.52
-0.3	-0.003	-0.002	-84.8	112.2	11.518
-0.2	-0.008	-0.002	-82.4	114.6	11.516
-0.1	-0.006	-0.002	-78.5	118.5	11.512
0	-0.006	-0.002	-74.9	122.1	11.508

0.01M Fe as Iron Oxide NaCl salt bridge
Copper pipe working electrode Replicate #1

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			272.9	469.9	6.502
0	-0.083	-0.067	185.5	382.5	6.231
-0.1	-0.011	-0.001	187.9	384.9	6.208
-0.2	-0.011	-0.001	189.2	386.2	5.201
-0.3	0.003	-0.001	192.4	389.4	6.187
-0.4	0.011	0.001	193.6	390.6	6.183
-0.5	0.024	0.003	196.8	393.8	6.192
-0.6	0.007	0.003	199.9	396.9	6.206
-0.7	0.008	0.004	201.9	398.9	6.213
-0.8	0.009	0.004	203.7	400.7	6.227
-0.9	0.014	0.005	205.6	402.6	6.252
-1	0.026	0.006	206.5	403.5	6.273
-1.1	0.077	0.007	210	407	6.279
-1.2	0.022	0.008	211.6	408.6	6.323
-1.3	0.04	0.013	196.7	393.7	6.569
-1.4	0.039	0.03	357	554	10.348
-1.5	0.134	0.061	358.4	555.4	10.428
-1.6	0.163	0.08	375.2	572.2	10.522
-1.7	0.151	0.127	368	565	10.785
-1.8	0.215	0.19	366.2	563.2	10.979
-1.9	0.306	0.291	363.7	560.7	11.09
-2	0.388	0.375	330.7	527.7	11.322
-1.9	0.294	0.286	321.2	518.2	11.344
-1.8	0.232	0.221	327	524	11.397
-1.7	0.18	0.155	325.3	522.3	11.409
-1.6	0.12	0.093	325.6	522.6	11.402
-1.5	0.271	0.049	330.2	527.2	11.421
-1.4	0.262	0.029	335.4	532.4	11.418
-1.3	0.029	0.017	338.2	535.2	11.419
-1.2	0.026	0.011	349.9	546.9	11.413
-1.1	0.14	0.011	352.7	549.7	11.411
-1	0.06	0.009	357.3	554.3	11.408
-0.9	0.031	0.008	362.2	559.2	11.404
-0.8	0.04	0.008	365	562	11.39
-0.7	0.025	0.007	369.2	566.2	11.386
-0.6	0.013	0.006	375.1	572.1	11.379
-0.5	0.007	0.005	376.9	573.9	11.378
-0.4	0.003	0.003	382.9	579.9	11.372
-0.3	0.007	0.003	384.3	581.3	11.37
-0.2	0.003	0.003	386.1	583.1	11.368
-0.1	0	0	387.3	584.3	11.366
0	-0.003	-0.009	400.4	597.4	11.318

0.01M Fe as Iron Oxide NaCl salt bridge

Copper pipe working electrode Replicate #2

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			257	454	6.183
0	-0.091	-0.085	177	374	6.112
-0.1	-0.031	-0.023	165.9	362.9	6.234
-0.2	-0.001	-0.001	171.3	368.3	6.358
-0.3	0.003	0.001	178.7	375.7	6.456
-0.4	0.007	0.003	182.3	379.3	6.527
-0.5	0.008	0.005	185.5	382.5	6.667
-0.6	0.017	0.007	187.9	384.9	6.708
-0.7	0.031	0.008	188.3	385.3	6.646
-0.8	0.021	0.008	186.4	383.4	6.586
-0.9	0.017	0.01	186.8	383.8	6.525
-1	0.028	0.011	182.7	379.7	6.612
-1.1	0.389	0.013	168.3	365.3	7.021
-1.2	0.187	0.017	159.6	356.6	7.862
-1.3	0.186	0.033	80	277	8.822
-1.4	0.082	0.046	121.3	318.3	9.43
-1.5	0.215	0.079	75.1	272.1	10.022
-1.6	0.16	0.135	290	487	10.51
-1.7	0.325	0.207	312.5	509.5	10.687
-1.8	0.305	0.296	334	531	11.079
-1.9	0.418	0.389	343.4	540.4	11.217
-2	0.553	0.518	335.4	532.4	11.272
-1.9	0.593	0.445	321.8	518.8	11.297
-1.8	0.419	0.385	305.7	502.7	11.357
-1.7	0.402	0.318	312.8	509.8	11.362
-1.6	0.264	0.232	314.9	511.9	11.368
-1.5	0.165	0.124	317.7	514.7	11.37
-1.4	0.301	0.087	322.1	519.1	11.369
-1.3	0.676	0.047	326.6	523.6	11.367
-1.2	0.621	0.033	330.7	527.7	11.366
-1.1	0.146	0.025	337.8	534.8	11.362
-1	0.456	0.025	340.8	537.8	11.36
-0.9	0.071	0.023	344.2	541.2	11.359
-0.8	0.175	0.023	346.6	543.6	11.357
-0.7	0.095	0.022	350.1	547.1	11.353
-0.6	0.065	0.021	520	717	11.352
-0.5	0.029	0.017	353.5	550.5	11.35
-0.4	0.035	0.013	355.5	552.5	11.348
-0.3	0.025	0.01	357.5	554.5	11.345
-0.2	0.007	0.007	359.2	556.2	11.343
-0.1	0.001	0.001	365.9	562.9	11.335
0	-0.008	0.001	372.8	569.8	11.323

0.01M Fe as Iron Oxide KNO3 salt bridge
Carbon rod working electrode Replicate #1

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			319.4	516.4	7.894
0	-0.003	-0.001	303.5	500.5	7.754
-0.1	0	-0.001	298	495	7.694
-0.2	0.004	0	295.1	492.1	7.654
-0.3	0.006	0.001	291.1	488.1	7.664
-0.4	0.008	0.003	286.6	483.6	7.708
-0.5	0.011	0.005	275.3	472.3	7.858
-0.6	0.039	0.006	257	454	8.313
-0.7	0.029	0.008	255.9	452.9	8.469
-0.8	0.031	0.008	277.8	474.8	8.779
-0.9	0.05	0.011	304.3	501.3	8.924
-1	0.057	0.009	351	548	9.155
-1.1	0.057	0.011	427.5	624.5	9.448
-1.2	0.151	0.021	448.2	645.2	9.511
-1.3	0.126	0.029	456.5	653.5	9.673
-1.4	0.061	0.042	450	647	9.835
-1.5	0.083	0.039	436.5	633.5	10.057
-1.6	0.081	0.056	404.6	601.6	10.3
-1.7	0.105	0.065	390	587	10.411
-1.8	0.098	0.06	365	562	10.502
-1.9	0.171	0.075	346.5	543.5	10.567
-2	0.136	0.523	68.7	265.7	11.245
-1.9	0.479	0.479	28.6	225.6	11.394
-1.8	0.436	0.386	10.8	207.8	11.484
-1.7	0.323	0.29	-12.4	184.6	11.585
-1.6	0.254	0.211	-46.8	150.2	11.766
-1.5	0.713	0.155	-43.8	153.2	11.762
-1.4	0.151	0.099	-44.6	152.4	11.775
-1.3	0.103	0.059	-41.9	155.1	11.776
-1.2	0.049	0.032	-39.8	157.2	11.778
-1.1	0.021	0.011	-37.7	159.3	11.779
-1	0.059	0.004	-35	162	11.777
-0.9	0.005	0.002	-30.6	166.4	11.773
-0.8	0.031	0.001	-28.6	168.4	11.771
-0.7	0.005	0.001	-26.1	170.9	11.769
-0.6	0.001	0.001	-21	176	11.761
-0.5	0.003	0.001	-19.5	177.5	11.757
-0.4	0.001	0	-19.6	177.4	11.753
-0.3	-0.001	-0.001	-19.9	177.1	11.751
-0.2	-0.003	-0.001	-19.5	177.5	11.749
-0.1	-0.008	-0.002	-19	178	11.748
0	-0.005	-0.001	-15.1	181.9	11.74

0.01M Fe as Iron Oxide
KNO3 salt bridge
Carbon rod working electrode
Replicate #2

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			259.8	456.8	5.77
0	-0.099	-0.001	31.1	228.1	8.855
-0.1	-0.001	-0.001	29.4	226.4	8.832
-0.2	0.001	0.001	30.6	227.6	8.813
-0.3	0.001	0	37.3	234.3	8.797
-0.4	0.013	0.001	40.4	237.4	8.802
-0.5	0.003	0.001	43.4	240.4	8.852
-0.6	0.008	0.002	48.2	245.2	8.95
-0.7	0.012	0.001	53.5	250.5	9.056
-0.8	0.009	0.002	58	255	9.148
-0.9	0.035	0.003	60.1	257.1	9.22
-1	0.011	0.003	63.3	260.3	9.302
-1.1	0.014	0.004	69.1	266.1	9.398
-1.2	0.03	0.008	68.4	265.4	9.633
-1.3	0.023	0.016	66.2	263.2	9.797
-1.4	0.037	0.031	46	243	10.209
-1.5	0.059	0.049	16.5	213.5	10.479
-1.6	0.085	0.075	-19.5	177.5	10.877
-1.7	0.399	0.103	-35	162	11.101
-1.8	0.201	0.135	-46.1	150.9	11.276
-1.9	0.227	0.173	-55.3	141.7	11.365
-2	0.243	0.213	-68.3	128.7	11.476
-1.9	0.19	0.183	-70.2	126.8	11.538
-1.8	0.187	0.147	-59.6	137.4	11.574
-1.7	0.16	0.117	-70.8	126.2	11.713
-1.6	0.111	0.089	-69.7	127.3	11.717
-1.5	0.075	0.061	-68	129	11.718
-1.4	0.055	0.037	-65.2	131.8	11.722
-1.3	0.031	0.024	-63.3	133.7	11.725
-1.2	0.026	0.013	-60.1	136.9	11.724
-1.1	0.011	0.005	-56.5	140.5	11.722
-1	0.01	0.002	-51	146	11.717
-0.9	0.01	0.001	-42.8	154.2	11.71
-0.8	0.005	0.001	-38.5	158.5	11.707
-0.7	0.003	0.001	-36.8	160.2	11.704
-0.6	0.025	0.001	-35.3	161.7	11.703
-0.5	0	0.001	-25.4	171.6	11.695
-0.4	0	0	-20.1	176.9	11.69
-0.3	-0.003	-0.001	-18.2	178.8	11.688
-0.2	-0.011	-0.001	-13.4	183.6	11.685
-0.1	-0.003	-0.001	-11.6	185.4	11.683
0	-0.005	-0.001	-3.6	193.4	11.669

0.006M Fe as Iron Nitrate KNO3 salt bridge
Copper pipe working electrode Replicate #1

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			590.9	787.9	2.752
0	-0.086	-0.056	569.6	766.6	2.753
-0.1	-0.004	-0.004	569.1	766.1	2.736
-0.2	0.126	0.001	568.6	765.6	2.72
-0.3	0.015	0.003	588.2	785.2	2.712
-0.4	0.01	0.002	567.3	764.3	2.694
-0.5	0.008	0.001	565.6	762.6	2.673
-0.6	0.005	0.001	564.7	761.7	2.655
-0.7	0.011	0.003	564.7	761.7	2.634
-0.8	0.023	0.005	564.7	761.7	2.627
-0.9	0.028	0.008	564.5	761.5	2.618
-1	0.059	0.013	564.4	761.4	2.611
-1.1	0.043	0.018	562.4	759.4	2.59
-1.2	0.177	0.032	556.9	753.9	2.573
-1.3	0.095	0.038	547.4	744.4	2.561
-1.4	0.138	0.046	540.7	737.7	2.551
-1.5	0.132	0.239	525.9	722.9	2.726
-1.6	0.533	0.291	517	714	2.745
-1.7	0.552	0.259	477.6	674.6	2.922
-1.8	0.513	0.338	49.3	246.3	7.933
-1.9	0.632	0.419	-7.7	189.3	10.302
-2	0.608	0.709	-45.5	151.5	11.344
-1.9	0.933	0.553	-57.4	139.6	11.473
-1.8	0.882	0.605	-52.6	144.4	11.581
-1.7	0.743	0.526	-42.8	154.2	11.633
-1.6	0.692	0.43	-40.5	156.5	11.623
-1.5	0.403	0.3	-34.5	162.5	11.624
-1.4	0.323	0.204	-23.4	173.6	11.642
-1.3	0.189	0.128	-3.4	193.6	11.631
-1.2	0.152	0.081	10.3	207.3	11.623
-1.1	0.104	0.045	16.2	213.2	11.621
-1	0.553	0.026	24.6	221.6	11.614
-0.9	35	0.011	35	232	11.601
-0.8	101.8	0.004	101.8	298.8	11.414
-0.7	102.2	0.003	102.2	299.2	11.406
-0.6	102.7	0.002	102.7	299.7	11.402
-0.5	103	0.002	103	300	11.392
-0.4	101.8	0.001	101.8	298.8	11.384
-0.3	100.1	0.001	100.1	297.1	11.378
-0.2	96.7	0	96.7	293.7	11.356
-0.1	97	-0.001	97	294	11.345
0	101.2	-0.001	101.2	298.2	11.318

0.006M Fe as Iron Nitrate KNO3 salt bridge
Copper pipe working electrode Replicate #2

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			544	741	2.306
0	-0.025	-0.195	221	418	3.32
-0.1	-0.056	-0.042	224	421	4.15
-0.2	0.028	0.025	225.8	422.8	4.265
-0.3	114	0.05	227.8	424.8	4.287
-0.4	0.068	0.049	229.7	426.7	4.298
-0.5	0.074	0.04	230.6	427.6	4.298
-0.6	0.062	0.039	232.4	429.4	4.287
-0.7	0.08	0.043	234.1	431.1	4.274
-0.8	0.085	0.046	234.8	431.8	4.279
-0.9	0.12	0.047	236.2	433.2	4.317
-1	0.183	0.07	237.7	434.7	4.335
-1.1	0.317	0.16	238.6	435.6	4.357
-1.2	0.24	0.154	239.4	436.4	4.365
-1.3	0.304	0.183	237.1	434.1	4.405
-1.4	0.306	0.202	229.1	426.1	4.546
-1.5	0.375	0.255	219.2	416.2	4.821
-1.6	0.453	0.284	212.9	409.9	5.132
-1.7	0.61	0.39	-54.4	142.6	9.304
-1.8	0.805	0.45	-78.3	118.7	10.329
-1.9	0.637	0.434	-83.2	113.8	10.933
-2	0.625	0.504	-63.2	133.8	11.188
-1.9	0.545	0.403	-58.7	138.3	11.214
-1.8	0.593	0.365	-56.2	140.8	11.255
-1.7	0.428	0.328	-54.4	142.6	11.298
-1.6	0.36	0.293	-52	145	11.329
-1.5	0.305	0.254	-49.3	147.7	11.344
-1.4	0.238	0.209	-46.2	150.8	11.355
-1.3	0.174	0.158	-44.4	152.6	11.364
-1.2	0.13	0.107	-41.4	155.6	11.362
-1.1	0.098	0.067	-38.4	158.6	11.365
-1	0.054	0.04	-35.4	161.6	11.359
-0.9	0.081	0.023	-15.4	181.6	11.296
-0.8	0.077	0.021	-12.6	184.4	11.286
-0.7	0.164	0.016	-10.9	186.1	11.282
-0.6	0.054	0.014	-9.3	187.7	11.275
-0.5	0.042	0.014	-8.2	188.8	11.272
-0.4	0.014	0.012	-6.6	190.4	11.264
-0.3	0.006	0.01	-4.8	192.2	11.258
-0.2	0.004	0.008	0.5	197.5	11.236
-0.1	0.002	0.006	1.3	198.3	11.233
0	-0.01	0.005	2	199	11.231

0.01M Fe as Iron Oxide KNO3 salt bridge
Copper pipe working electrode Replicate #1

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			184.6	381.6	6.797
0	-0.023	-0.018	140.7	337.7	6.797
-0.1	0.004	0.005	139.6	336.6	6.767
-0.2	0.009	0.009	143.3	340.3	6.727
-0.3	14	0.011	143.8	340.8	6.734
-0.4	0.017	0.012	141.7	338.7	6.682
-0.5	0.019	0.015	125	322	7.02
-0.6	0.025	0.015	95.7	292.7	7.456
-0.7	0.063	0.016	80.2	277.2	8.283
-0.8	0.053	0.019	75.5	272.5	8.351
-0.9	0.087	0.031	64.2	261.2	8.513
-1	0.073	0.047	72.4	269.4	9.134
-1.1	0.227	0.076	89.6	286.6	9.52
-1.2	0.18	0.082	103.1	300.1	9.945
-1.3	0.301	0.091	136.4	333.4	10.757
-1.4	0.217	0.1	146.4	343.4	10.89
-1.5	0.42	0.11	140.2	337.2	11.205
-1.6	0.346	0.164	141.2	338.2	11.199
-1.7	0.28	0.191	144.7	341.7	11.227
-1.8	0.518	0.261	135.3	332.3	11.296
-1.9	0.499	0.321	122	319	11.367
-2	0.881	0.416	79.7	276.7	11.487
-1.9	0.406	0.328	64.5	261.5	11.537
-1.8	0.611	0.271	69.7	266.7	11.536
-1.7	0.429	0.217	74	271	11.529
-1.6	0.343	0.18	74.7	271.7	11.53
-1.5	0.391	0.171	78.3	275.3	11.55
-1.4	0.224	0.125	85.4	282.4	11.549
-1.3	0.172	0.116	91.1	288.1	11.557
-1.2	0.117	0.083	96.1	293.1	11.562
-1.1	0.093	0.055	102.7	299.7	11.564
-1	0.079	0.04	108.1	305.1	11.566
-0.9	0.273	0.031	114.8	311.8	11.566
-0.8	0.147	0.024	118.4	315.4	11.565
-0.7	0.039	0.019	122.6	319.6	11.564
-0.6	0.057	0.017	126.5	323.5	11.561
-0.5	0.042	0.015	133.1	330.1	11.558
-0.4	0.02	0.015	135.5	332.5	11.555
-0.3	0.013	0.012	137.2	334.2	11.553
-0.2	0.009	0.009	139.3	336.3	11.552
-0.1	0.008	0.009	141.3	338.3	11.551
0	0.002	0.007	144	341	11.547

0.01M Fe as Iron Oxide
Copper pipe working electrode

KNO3 salt bridge
Replicate #2

Eapplied (V)	Current (mA)	Current t=1min (mA)	Eh (mV)	Eh v. NHE (mV)	pH
0			197.6	394.6	8.093
0	-0.021	-0.002	143.2	340.2	8.041
-0.1	0.004	0.006	136.4	333.4	8.013
-0.2	0.01	0.009	135.6	332.6	7.977
-0.3	0.012	0.011	132.7	329.7	7.971
-0.4	0.018	0.014	126.5	323.5	8.002
-0.5	0.031	0.017	117.3	314.3	8.077
-0.6	0.03	0.019	107.2	304.2	8.192
-0.7	0.051	0.019	85.5	282.5	8.47
-0.8	0.043	0.022	82	279	8.676
-0.9	0.055	0.037	65.5	262.5	8.956
-1	0.095	0.053	63	260	9.427
-1.1	0.106	0.065	79.4	276.4	9.73
-1.2	0.128	0.061	120.6	317.6	9.905
-1.3	0.207	0.081	150.1	347.1	10.06
-1.4	0.297	0.123	210	407	10.163
-1.5	0.312	0.125	228.3	425.3	10.293
-1.6	0.28	0.131	230.3	427.3	10.423
-1.7	0.336	0.181	221.4	418.4	10.585
-1.8	0.33	0.241	200.1	397.1	10.794
-1.9	0.648	0.302	186.1	383.1	10.929
-2	0.539	0.297	145.8	342.8	10.983
-1.9	0.435	0.237	145.6	342.6	10.994
-1.8	0.356	0.237	140.8	337.8	11.034
-1.7	0.369	0.187	107	304	11.164
-1.6	0.289	0.16	101.7	298.7	11.192
-1.5	0.235	0.135	99	296	11.205
-1.4	0.205	0.107	99.8	296.8	11.222
-1.3	0.155	0.091	105	302	11.244
-1.2	0.091	0.067	107.9	304.9	11.253
-1.1	0.171	0.044	128.5	325.5	11.253
-1	0.061	0.037	133.4	330.4	11.25
-0.9	0.189	0.026	142.6	339.6	11.246
-0.8	0.032	0.02	147.7	344.7	11.238
-0.7	0.031	0.017	158.5	355.5	11.229
-0.6	0.084	0.015	166.2	363.2	11.227
-0.5	0.038	0.015	168.8	365.8	11.223
-0.4	0.013	0.013	170.9	367.9	11.218
-0.3	0.012	0.012	173.4	370.4	11.218
-0.2	0.008	0.009	175.7	372.7	11.216
-0.1	0.008	0.009	180.6	377.6	11.211
0	0.005	0.008	182.8	379.8	11.135

APPENDIX B

ELECTROLYTIC OXIDATION/REDUCTION STUDIES USING IRON NITRATE

20-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			627.3	824.3	2.433	546
0	0	1.2				
0	0	1.2				
0.5	0	1.2	594.2	791.2	2.461	541
1	0	1.1	580.8	777.8	2.471	528
1.5	0	1.1	575.4	772.4	2.336	526

24-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			653.6	850.6	2.392	444
0	0	1.1				
0	0	1.1				
0.5	0	1.1	597.8	794.8	2.382	480
1	0	1.1	583.8	780.8	2.39	516
1.5	0	1.1	574.5	771.5	2.397	541

11-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			654.6	851.6	2.652	542
0	0	1.1				
0	-200	3.7				
2	-200	3.6	546.8	743.8	2.433	554
4	-200	2.7	528.8	725.8	2.421	431
6	-200	1.6	517.4	714.4	2.369	582

12-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			646.9	843.9	2.422	521
0	0	1.3				
0	-200	3.7				
2	-200	3.7	543.5	740.5	2.418	562
4	-200	3	524	721	2.368	532
6	-200	1.8	512	709	2.302	500

15-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			649.9	846.9	2.971	504
0	0	0.8				
0	-1200	10.9				
2	-1200	7.2	588.2	785.2	2.608	520
4	-1200	5.7	594	791	2.498	525
6	-1200	5.1	579.3	776.3	2.53	525

22-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			628.3	825.3	2.44	546
0	0	0.8				
0	-1200	15				
2	-1200	9	572.8	769.8	2.526	555
4	-1200	9	558.6	755.6	2.558	537
6	-1200	6.2	567.8	764.8	2.501	479

16-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			638.6	835.6	2.268	535
0	0	0.8				
0	-1400	18				
2	-1400	8.9	580	777	2.392	507
4	-1400	7.8	586.9	783.9	2.373	464
6	-1400	4.9	585.5	782.5	2.371	480

17-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			623.6	820.6	2.461	539
0	0	0.83				
0	-1400	15				
2	-1400	10	583.1	780.1	2.65	536
4	-1400	6.8	582.6	779.6	2.621	527
6	-1400	5.5	584.5	781.5	2.594	535

19-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			612.4	809.4	2.48	520
0	0	1.1				
0	-1600	32				
2	-1600	66	550.9	747.9	2.807	129
4	-1600	106	63	260	8.184	12
6	-1600	55	-77	120	9.552	7

23-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			627.4	824.4	2.383	531
0	0	0.8				
0	-1600	32				
2	-1600	60	554.2	751.2	2.777	497
4	-1600	55	562.6	759.6	2.615	369
6	-1600	65	-85.3	111.7	10.128	0

25-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			629.1	826.1	2.409	531
0	0	0.8				
0	-1800	80				
0.5	-1800	112	589.9	786.9	2.526	446
1	-1800	90	584.8	781.8	2.574	423
1.5	-1800	92	555.5	752.5	2.796	235

30-May-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)
0			643	840	2.348	1349
0	0	0.8				
0	-1800	111				
0.75	-1800	108	567.4	764.4	2.733	1126
1.5	-1800		326.7	523.7	4.211	5
2.25	-1800					

APPENDIX C

ELECTROLYTIC OXIDATION/REDUCTION STUDIES USING ARSENIC CONTAMINATED SOIL

1-Jul-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)	As (mg/L)	Cu(mg/L)
0			110	307	6.706	12.4	1.65	0.216
0	0	0.1						
0	0	0.1						
0.5	0	0.1	94.3	291.3	6.789	7.61	0.271	0.068
1	0	0	93.9	290.9	6.669	11.3	1.26	0.166
1.5	0	0	104.2	301.2	7.085	5.33	0.324	0.059

1-Jul-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)	As(mg/L)	Cu(mg/L)
0			116.7	313.7	6.732	11.8	0.279	0.138
0	0	0						
0	0	0						
0.5	0	0	101.2	298.2	6.927	7.32	0.341	0.0561
1	0	0.1	95.5	292.5	7.029	5.38	0.27	0.0327
1.5	0	0	88.7	285.7	7.029	7.27	0.346	0.058

2-Jun-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)	As (mg/L)	Cu(mg/L)
0			108	305	6.229	0.611	0.769	0.0279
0	0	3.2						
0	-1200	16						
2	-1200	2.3	47.8	244.8	6.254	1.61	1.19	0.0432
4	-1200	2.3	39.2	236.2	6.516	0.633	1.54	0.03
6	-1200	2.4	27	224	6.545	1.65	1.84	0.0463

5-Jun-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)	As (mg/L)	Cu(mg/L)
0			172.2	369.2	6.467	6.43	2.7	0.134
0	0	0						
0	-1200	7.9						
2	-1200	7.5	-0.5	196.5	7.487	2.95	2.88	0.0573
4	-1200	7.7	-24.7	172.3	7.977	4.14	4.06	0.11
6	-1200	5.8	-24.3	172.7	8.289	4.46	4.23	0.0955

7-Jun-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)	As (mg/L)	Cu(mg/L)
0			92.2	289.2	6.64	3.05	1.38	0.0329
0	0	-0.4						
0	-1400	41						
2	-1400	37.5	-38.5	158.5	9.741	6.42	4.28	0.117
4	-1400	43	-59.8	137.2	10.634	12.9	4.87	0.178
6	-1400	44	-104.5	92.5	11.293	15.4	5.01	0.23

8-Jun-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)	As (mg/L)	Cu(mg/L)
0			130.7	327.7	6.612	3.15	0.413	0.0135
0	0	-0.1						
0	-1400	35						
2	-1400	39	17.3	214.3	9.483	4.76	1.84	0.051
4	-1400	19	-46.2	150.8	9.852	5.5	2.47	0.0964
6	-1400	44	-97.7	99.3	11.063	7.04	2.66	0.183

3-Jun-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)	As (mg/L)	Cu(mg/L)
0			119	316	6.084	0.667	1.22	0.025
0	0	-0.1						
0	-1600	122						
2	-1600	127	-110	87	11.531	13.2	4.25	0.459
4	-1600	124	-138.1	58.9	12.11	12.4	3.46	0.324
6	-1600	127	-145	52	12.242	13.6	3.34	0.262

4-Jul-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)	As(mg/L)	Cu(mg/L)
0			134.7	331.7	6.634	16.3	2.58	0.162
0	0							
0	-1600	36						
2	-1600	44	-50.7	146.3	9.959	21.5	2	0.25
4	-1600	45.5	-73.7	123.3	10.745	5.86	1.27	0.0734
6	-1600	33.8	-68.7	128.3	10.667	9.89	0.326	0.105

5-Jul-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)	As(mg/L)	Cu(mg/L)
0			131.2	328.2	6.808	5.31	0.414	0.0462
0	0							
0	-1800	86						
2	-1800	147	-145.9	51.1	11.785	13.9	2.09	0.26
4	-1800	137	-161.5	35.5	12.17	10.9	2.56	0.375
6	-1800	114	-164.4	32.6	11.773	12.1	3.27	0.432

6-Jul-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside	Fe (mg/L)	As(mg/L)	Cu(mg/L)
0			129.8	326.8	6.732	4.81	0.337	0.00774
0	0							
0	-1800	120						
2	-1800	193	-136.8	60.2	12.184	10.4	1.88	0.224
4	-1800	200	-133.1	63.9	12.56	11.5	1.78	0.226
6	-1800	159	-180.5	16.5	12.667	21.1	1.47	0.322

APPENDIX D

ELECTROLYTIC OXIDATION/REDUCTION STUDIES USING FURNACE SLAG

12-Jun-06 No EDTA

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-281.2	-84.2	12.422
0	0	0.8			
0	2000	-10.5			
2	2000	-9.6	-223.1	-26.1	12.157
4	2000	-6.6	-240.1	-43.1	12.09
6	2000	-5.6	-216.4	-19.4	11.87

12-Jun-06

Time (hr)	Fe (ug/L)	As (ug/L)	Cu (ug/L)	Sr (ug/L)	Ba (ug/L)
0	1110	7.8	29.6	1030	859
0					
0					
2	1090	5.97	4.03	934	738
4	1570	6.1	2.87	1030	802
6	1010	13.8	8.01	985	753

14-Jun-06 No EDTA

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-279.4	-82.4	12.088
0	0	201			
0	2000	-7			
2	2000	-3.7	-322.7	-125.7	11.452
4	2000	-3	-237.7	-40.7	11.224
6	2000	-2.5	-240.8	-43.8	11.205

14-Jun-06

Time (hr)	Fe (mg/L)	As (ug/L)	Cu (ug/L)	Sr (ug/L)	Ba (ug/L)
0	322	4.34	2.99	329	328
0					
0					
2	527	5.47	1.98	357	372
4	610	4.51	2.57	380	393
6	1400	9.88	3.81	493	497

2-Jul-06 No EDTA

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-306	-109	12.48
0	0				
0	1600	-4			
2	1600	-2.6	-303	-105.7	12.42
4	1600	-2.4	-305	-107.8	12.344
6	1600	-1.9	-300	-103.3	12.166

2-Jul-06

Time (hr)	Fe (mg/L)	As (ug/L)	Cu (ug/L)	Sr (ug/L)	Ba (ug/L)
0	796	1.96	24.6	927	797
0					
0					
2	753	2.61	7.38	983	856
4	1370	1.75	5.75	1020	898
6	934	1.38	2.28	1260	1090

3-Jul-06 No EDTA

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-246	-49.3	12.677
0	0				
0	1600	-4.9			
2	1600	-1.9	-207	-10.3	12.861
4	1600	-1.9	-213	-16.3	12.476
6	1600	-1.7	-246	-48.8	12.524

3-Jul-06

Time (hr)	Fe (mg/L)	As(ug/L)	Cu(ug/L)	Sr (ug/L)	Ba(ug/L)
0	828	4.03	4.24	679	630
0					
0					
2	872	3.7	3.81	755	702
4	898	4.36	2.26	788	732
6	940	3.12	1.91	856	801

9-Jul-06 No EDTA

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-267.4	-70.4	12.935
0	0				
0	0	2			
2	0	0.2	-284.2	-87.2	12.896
4	0	0.1	-267	-70	12.923
6	0	0.1	-274.2	-77.2	12.819

9-Jul-06

Time (hr)	Fe (mg/L)	As(ug/L)	Cu(ug/L)	Sr (ug/L)	Ba(ug/L)
0	1080	7.1	28.1	1300	1060
0					
0					
2	993	5.18	8.49	1260	1030
4	888	2.28	3.68	1290	1060
6	993	4.19	3.56	1710	1410

9-Jul-06 No EDTA

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-264	-67	12.935
0	0				
0	0	1.3			
2	0	0.1	-271.7	-74.7	12.952
4	0	0.1	-286.9	-89.9	12.876
6	0	0	-286.6	-89.6	12.919

9-Jul-06

Time (hr)	Fe (mg/L)	As(ug/L)	Cu(ug/L)	Sr (ug/L)	Ba(ug/L)
0	1000	0.77	1.58	1390	1150
0					
0					
2	1600	2.07	3.78	1510	1250
4	1060	2.73	0.209	1460	1220
6	1040	1.42	0.235	1470	1210

28-Jun-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-325.8	-128.8	11.358
0	0	1.5			
0	1600	-17.1			
2	1600	-7.5	-408.2	-211.2	10.994
4	1600	-5.4	-410.6	-213.6	10.972
6	1600	-4.1	-431.2	-234.2	10.999

28-Jun-06

Time (hr)	Fe (mg/L)	As(ug/L)	Cu(ug/L)	Sr (ug/L)	Ba(ug/L)
0	3990	1.67	8.83	1260	177
0					
0					
2	3910	0.934	14.5	1310	211
4	3720	0.908	15.6	1320	226
6	3680	0.816	17.3	1370	240

29-Jun-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-310.1	-113.1	11.474
0	0	1.5			
0	1600	-75			
2	1600	-4.1	-439.3	-242.3	10.129
4	1600	-2.3	-443.8	-246.8	10.721
6	1600	-2.8	-204.6	-7.6	10.863

29-Jun-06

Time (hr)	Fe (mg/L)	As(ug/L)	Cu(ug/L)	Sr (ug/L)	Ba(ug/L)
0	4210	0.89	27.9	1380	176
0					
0					
2	3620	1.15	6.3	1430	248
4	4060	0.913	10.6	1580	246
6	3760	2.63	39.2	1470	233

1-Jul-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-287.9	-90.9	11.529
0	0	4.2			
0	0	0.3			
2	0	0.3	-317.3	-120.3	11.444
4	0	0.8	-283.5	-86.5	11.507
6	0	0.1	-308.3	-111.3	11.429

1-Jul-06

Time (hr)	Fe (mg/L)	As(ug/L)	Cu(ug/L)	Sr (ug/L)	Ba(ug/L)
0	3560	2.18	20.1	1300	184
0					
0					
2	3420	1.44	11.9	1300	194
4	3570	8.13	25.5	1330	207
6	3490	2.04	19.9	1330	209

9-Jul-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-259.4	-62.4	12.035
0	0				
0	0	0.2			
2	0	0	-263.4	-66.4	11.958
4	0	0	-252	-55	11.985
6	0	0	-256.5	-59.5	12.045

9-Jul-06

Time (hr)	Fe (mg/L)	As(ug/L)	Cu(ug/L)	Sr (ug/L)	Ba(ug/L)
0	4210	0.201	17.2	1350	195
0					
0					
2	3970	0.22	9.2	1300	197
4	3910	1.39	10.3	1320	208
6	3490	7.19	29.1	1170	190

7-Jul-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-321.3	-124.3	11.861
0	0				
0	2000	-20			
2	2000	-12.5	-310.1	-113.1	11.454
4	2000	-10.3	-461.1	-264.1	11.06
6	2000	-9	-279.1	-82.1	11.183

7-Jul-06

Time (hr)	Fe (mg/L)	As(ug/L)	Cu(ug/L)	Sr (ug/L)	Ba(ug/L)
0	4010	0.0673	4.4	1300	181
0					
0					
2	4030	1.12	6.99	1410	239
4	3900	0.287	9.56	1470	264
6	3860	0.722	12.4	1510	277

8-Jul-06

Time (hr)	Eapplied (mA)	Current (mA)	Eh outside	Eh v. NHE	pH outside
0			-287.8	-90.8	11.958
0	0	2.3			
0	2000	-12.8			
2	2000	-11.1	-294.5	-97.5	11.515
4	2000	-9.2	-305	-108	11.544
6	2000	-8.5	-300.6	-103.6	11.497

8-Jul-06

Time (hr)	Fe (mg/L)	As(ug/L)	Cu(ug/L)	Sr (ug/L)	Ba(ug/L)
0	3880	1.41	32.9	1250	146
0					
0					
2	4180	0.001	17.2	1440	211
4	3830	1.41	30.9	1370	212
6	4300	0.001	28.4	1450	232

REFERENCES

(1977). Arsenic. Washington, D.C., Printing and Publishing Office.

Acar, Y. B., R. J. Gale, et al. (1995). "Electrokinetic remediation: Basics and technology status." Journal of Hazardous Materials **40**: 117-137.

Ahmann, D., L. R. Krumholz, et al. (1997). "Microbial Mobilization of Arsenic from Sediments of the Aberjona Watershed." Environmental Science & Technology **31**: 2923-2930.

Ahmann, D., A. L. Roberts, et al. (1994). "Microbe grows by reducing arsenic." Nature **371**(27): 750.

Alloway, B. J. (1995). Heavy Metals in Soils. London, Blackie Academic & Professional.

Anderson, G. L., J. Williams, et al. (1992). "The purification and characterization of arsenate oxidase from *Alcaligenes faecalis*, a molybdenum-containing hydroxylase." The Journal of Biological Chemistry **267**(33): 23674-23682.

Bard, A. J. and L. R. Faulkner (2001). Electrochemical Methods: Fundamentals and Applications. New York, John Wiley & Sons, Inc.

Belzile, N. and A. Tessier (1990). "Interactions between arsenic and iron oxyhydroxides in lacustrine sediments." Geochimica et Cosmochimica Acta **54**: 103-109.

Bennett, B. and M. V. Dudas (2003). "Release of arsenic and molybdenum by reductive dissolution of iron oxides in a soil with enriched levels of native arsenic." Journal of Environmental Engineering and Science **2**(4): 265-272.

Bland, B. and D. Rolls (1998). Weathering An Introduction to the Scientific Principles. New York, Arnold Publishing.

Blum, J. S., A. B. Bindi, et al. (1998). "*Bacillus arsenicoselenatis*, sp. nov., and *Bacillus selenitireducens*, sp. nov.: two haloalkaliphiles from Mono Lake, California that respire oxyanions of selenium and arsenic." Arch Microbiol **171**: 19-30.

Bohn, H. L., B. L. McNeal, et al. (1985). Soil Chemistry. New York, John Wiley & Sons.

Buresh, R. J. and W. H. J. Patrick (1981). "Nitrate reduction to ammonium and organic nitrogen in an estuarine sediment." Soil Biol Biochem **13**: 279-283.

Carbonell-Barrachina, A., R. D. Delaune, et al. (2002). "Phosphogypsum chemistry under highly anoxic conditions." Waste Management **22**: 657-665.

Chatain, V. (2004). Caracterisation de la mobilisation potentielle de l'arsenic det d'autres constituants inorganiques presents dans les sols issus d'un site minier aurifere. Lyon, INSA of Lyon, France. **PhD**.

Chatain, V., R. Bayard, et al. (2005). "Effect of indegenous bacterial activity on arsenic mobilization under anaerobic conditions." Environment International **31**: 221-226.

Chatain, V., F. Sanchez, et al. (2003). "Arsenic Behavior in Mining Soil." Journal de Physique IV **107**.

Chatain, V., F. Sanchez, et al. (2005). "Effect of experimentally induced reducing conditions on the mobility of arsenic from a mining soil." Journal of Hazardous Materials **B122**: 119-128.

Chi, R., G. Zhu, et al. (2002). "Kinetics of Manganese Reduction Leaching from Weathered Rare-Earth Mud with Sodium Sulfite." Metallurgical and Materials Transactions **33B**: 41-46.

Christensen, I. V., A. J. Pedersen, et al. (2006). "Electrodialytic remediation of CCA-treated waste wood in a 2 m3 pilot plant." Science of The Total Environment **364**(1-3): 45.

Datta, N. C. (1981). "Chemistry of Iron(III) Oxides and Oxyhydroxides." Journal of Scientific and Industrial Research **40**: 571-583.

Davidson, G. R., S. J. Bennett, et al. (2005). "Trace elements in sediments of an aging reservoir in rural Mississippi: Potential for mobilization following dredging." Water, Air, and Soil Pollution **163**: 281-292.

Davranche, M. and J.-C. Bollinger (2000). "Heavy Metals Desorption from Synthesized and Natural Iron and Manganese Oxyhydroxides: Effect of Reductive Conditions." Journal of Colloid and Interface Science **227**: 531-539.

Davranche, M. and J.-C. Bollinger (2000). "Release of Metals from Iron Oxyhydroxides under Reductive Conditions: Effect of Metal/Solid Interactions." Journal of Colloid and Interface Science **232**: 165-173.

Davranche, M., J.-C. Bollinger, et al. (2003). "Effect of reductive conditions on metal mobility from wasteland solids: an example from the Mortagne-du-Nord site (France)." Applied Geochemistry **18**(3): 383-394.

de Vitre, R., N. Belzile, et al. (1991). "Speciation and Adsorption of Arsenic on Diagenetic Iron Oxyhydroxides." Limnology and Oceanography **36**(7): 1480-1485.

EPA, U. (1992). Method 1311 Toxicity Characteristic Leaching Procedure.

Ferguson, J. F. and J. Gavis (1972). "A review of the arsenic cycle in natural waters." Water Research **6**: 1259-1274.

Frankenberger, W. T. J., Ed. (2002). Environmental Chemistry of Arsenic. New York, Marcel Dekker, Inc.

Garrabrants, A. C. (2006). Personal Communication. Nashville.

Gosser, D. K. J. (1993). Cyclic Voltammetry Simulation and Analysis of Reaction Mechanisms. New York, VCH Publishers, Inc.

Grygar, T., J. Dedecek, et al. (2002). "Analysis of low concentration of free ferric oxides in clays by vis diffuse reflectance spectroscopy and voltammetry." Gelogica Carpathica **53**(2): 1-7.

Guha, H. (2004). "Biogeochemial influence on transport of chromium in manganese sediments: experimental and modeling approaches." Journal of Contaminant Hydrology **70**: 1-36.

Guo, T., R. D. DeLaune, et al. (1997). "The influence of sediment redox chemistry on chemically active forms of arsenic, cadmium, chromium, and zinc in estuarine sediment." Environment International **23**(3): 305-316.

Gupta, V. K., V. K. Saini, et al. (2005). "Adsorption of As(III) from aqueous solutions by iron oxide-coated sand." Journal of Colloid and Interface Science(288): 55-60.

Hanke, M. E. and Y. J. Katz (1943). "An Electrolytic Method for Controlling Oxidation-Reduction Potential and Its Application in the Study of Anaerobiosis."

Hansen, H. K., A. Rojo, et al. (2005). "Electrodialytic remediation of copper mine tailings." Journal of Hazardous Materials **117**(2-3): 179.

http://www.ijcambria.com "Electrochemical Electrode and Accessories." Date of access: July 20, 2006

Islam, F. S., A. G. Gault, et al. (2004). "Role of metal-reducing bacteria in arsenic release from Bengal delta sediments." Nature **430**: 68-71.

Jakobsen, M. R., J. Fritt-Rasmussen, et al. (2004). "Electrodialytic removal of cadmium from wastewater sludge." Journal of Hazardous Materials **106**(2-3): 127.

Jong, T. and D. L. Parry (2005). "Evaluation of the stability of arsenic immobilized by microbial sulfate reduction using TCLP extractions and long-term leaching techniques." Chemosphere **60**: 254-265.

Kheboian, C. and C. F. Bauer (1987). "Accuracy of Selective Extraction Procedures for Metal Speciation in Model Aquatic Sediments." Analytical Chemistry **59**(10): 1417-1423.

Knowles, F. C. and A. A. Benson (1983). "The biochemistry of arsenic." Trends in Biochemical Sciences **8**: 178-180.

Kosson, D. S., H. A. van der Sloot, et al. (2002). "An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials." Environmental Engineering Science **19**(3): 159-202.

Kumari, A. and K. A. Natarajan (2002). "Electrochemical aspects of leaching of ocean nodules in the presence and absence of microorganisms." International Journal of Mineral Processing **66**: 29-47.

Langmuir, D. (1997). Aqueous Environmental Geochemistry. Upper Saddle River, Prentice-Hall, Inc.

Lim, T. T., J. H. Tay, et al. (2004). "Changes in mobility and speciation of heavy metals in clay-amended incinerator fly ash." Environmental Geology **47**: 1-10.

Liu, C. X., Y. A. Gorby, et al. (2002). "Reduction kinetics of Fe(III), Co(III), U(VI) Cr(VI) and Tc(VII) in cultures of dissimilatory metal-reducing bacteria." Biotechnology And Bioengineering **80**(6): 637-649.

Macur, R. E., C. R. Jackson, et al. (2004). "Bacterial populations associated with the oxidation and reduction of arsenic in an unsaturated soil." Environmental Science & Technology **38**(1): 104-111.

Macy, J. M., J. M. Santini, et al. (2000). "Two new arsentate/sulfate-reducing bacteria: mechanisms of arsenate reduction." Arch Microbiol **173**: 49-57.

Manning, B. A. and S. Goldberg (1997). "Adsorption and Stability of Arsenic(III) at the Clay Mineral-Water Interface." Environmental Science & Technology **31**: 2005-2011.

Masscheleyn, P. H., R. D. Delaune, et al. (1990). "Transformations of Selenium As Affected by Sediment Oxidation-Reduction Potential and pH." Environmental Science & Technology **24**(1): 91-96.

Masscheleyn, P. H., R. D. Delaune, et al. (1991). "Effect of Redox Potential and pH on Arsenic Speciation and Solubility in a Contaminated Soil." Environmental Science & Technology **25**: 1414-1419.

Masscheleyn, P. H., R. D. Delaune, et al. (1991). "Effect of Redox Potential and pH on Arsenic Speciation and Solubility in a Contaminated Soil." Environmental Science & Technology **25**(8): 1414-1419.

Miller, D. M., T. Tang, et al. (1993). "Electrolytic Reduction of Soil Suspensions." Soil Science Society of America **57**: 356-360.

Miller, T. L. and M. J. Wolin (1974). "A Serum Bottle Modification of the Hungate Technique for Cultivation Obligate Anaerobes." Applied Microbiology **27**(5): 985-987.

Newman, D. K., E. K. Kennedy, et al. (1997). "Dissimilatory arsenate and sulfate reduction in *Desulotomaculm auripigmentum* sp. nov." Arch Microbiol **168**: 380-388.

Ng, J. C. (2005). "Environmental Contamination of Arsenic and its Toxicological Impact on Humans." Environmental Chemistry **2**(3): 146-160.

Niggemyer, A., S. Spring, et al. (2001). "Isolation and Characterization of a Novel As(V)-Reducing Bacterium: Implications for Arsenic Mobilization and the Genus *Desulfitobacterium*." Applied and Environmental Microbiology **67**(12): 5568-5580.

Niinae, M., N. Komatsu, et al. (1996). "Preferential leaching of cobalt, nickel and copper from cobalt-rich ferromanganese crusts with ammoniacal solutions using ammonium thiosulfate and ammonium sulfite as reducing agents." Hydrometallurgy **40**: 111-121.

Nirel, P. M. V. and F. M. M. Morel (1990). "Pitfalls of Sequential Extraction." Water Research **24**(8): 1055-1056.

Nystroem, G. M., A. J. Pedersen, et al. (2006). "The use of desorbing agents in electrodialytic remediation of harbour sediment." Science of The Total Environment **357**(1-3): 25.

Ollier, C. (1984). Weathering. Essex, Longman Group Limited.

Oremland, R. S., P. R. Dowdle, et al. (2000). "Bacterial dissimilatory reduction of arsenate and sulfate in meromictic Mono Lake, California." Geochimica et Cosmochimica Acta **64**(18): 3073-3084.

Oremland, R. S. and J. F. Stolz (2005). "Arsenic, microbes and contaminated aquifers." TRENDS in Microbiology **13**(2): 45-49.

Patrick, W. H. J., B. G. Williams, et al. (1973). "A simple system for controlling redox potential and pH in soil suspensions." Soil Science Society of America **37**: 331-332.

Pedersen, A. J. (2003). "Characterization and electrodialytic treatment of wood combustion fly ash for the removal of cadmium." Biomass and Bioenergy **25**(4): 447.

Pedersen, A. J., L. M. Ottosen, et al. (2005). "Electrodialytic removal of heavy metals from municipal solid waste incineration fly ash using ammonium citrate as assisting agent." Journal of Hazardous Materials **122**(1-2): 103.

Pickering, W. F. (1989). The competing roles of dissolution, sorption and complex formation in element mobilization. Weathering; its Products and Deposits Barto-Kyriadkidis. Athens, Theophrastus Publications, S.A. **1:** 259-305.

Pierce, M. L. and C. B. Moore (1981). "Adsorption of arsenite and arsenate on amorphous iron hydroxide." Water Research **16**: 1247-1253.

Plant, J. A., D. G. Kinniburgh, et al. (2003). Arsenic and Selenium. Environmental Geochemistry. B. S. Lollar. Oxford, Elsevier Ltd. **9:** 17-66.

Pourbaix, M. (1966). Atlas of electrochemical equilibria in aqueous solutions. Oxford, Pergamon Press.

Rennert, T. and T. Mansfeldt (2005). "Iron-cyanide complexes in soil under varying redox conditions: speciation, solubility and modelling." European Journal of Soil Science **56**: 527-536.

Rhine, D. E., C. D. Phelps, et al. (2006). "Anaerobic arsenite oxidation by novel denitrifying isolates." Environmental Microbiology **8**(5): 899-908.

Ribet, I., C. J. Ptacek, et al. (1995). "The potential for metal release by reductive dissolution of weathered mine tailings." Journal of Contaminant Hydrology **17**: 239-273.

Rojo, A., H. K. Hansen, et al. (2006). "Electrodialytic remediation of copper mine tailings: Comparing different operational conditions." Minerals Engineering **19**(5): 500.

Salmassi, T. M., J. J. Walker, et al. (2006). "Community and cultivation analysis of arsenite oxidizing biofilms at Hot Creek." Environmental Microbiology **8**(1): 50-59.

Sanchez, F., C. H. Mattus, et al. (2002). "Use of a New Leaching Test Framework for Evaluating Alternative Treatment Processes for Mercury-Contaminated Soils." Environmental Engineering Science **19**(4): 251-269.

Santini, J. M., L. I. Sly, et al. (2000). "A new chemolithoautotrophi arsenite-oxidizing bacterium isolated from a gold mine: phylogenetic, physiological, and preliminary biochemical studies." Applied and Environmental Microbiology **66**(1): 92-97.

Smolen, J. M., M. A. McLaughlin, et al. (2003). "Reductive dissolution of goethite and the subsequent transformation of 4-cyanonitrobenzene: Role of ascorbic acid and pH." Aquatic Sciences **65**: 308-315.

Snoeyink, V. L. and D. Jenkins (1980). Water Chemistry, John Wiley & Sons, Inc.

Stumm, W. and J. J. Morgan (1998). Aquatic Chemistry Chemical Equilibria and Rates in Natural Waters. New York, John Wiley & Sons, Inc.

Temple, J. L. (2003). Effect of reducing conditions on the release of inorganic contaminants from wastes and secondary materials. Civil and Environmental Engineering. Nashville, Vanderbilt University. **M.S.:** 108.

Tessier, A. and G. C. Campbell (1991). "Comment on "Pitfalls of sequential extractions" by P.M.V. Nirel and F.M.M. Morel, *Wat. Res.* **24**, 1055-1056 (1990)." Water Research **25**(1): 115-117.

Tessier, A., G. C. Campbell, et al. (1979). "Sequential Extraction Procedure for the Speciation of Particulate Trace Metals." Analytical Chemistry **51**(7): 844-851.

van der Sloot, H. A. (2002). "Characterization of the leaching behaviour of concrete mortars and of cement-stabilized wastes with different waste loading for long term environmental assessment." Waste Management **22**: 181-186.

van der Sloot, H. A. (2005). "End of black box approach? A step towards more sustainable landfills." Waste Management **25**: 461.

van der Sloot, H. A., D. Hoede, et al. (2001). "Leaching Behaviour of synthetic aggregates." Waste Management **21**: 221-228.

van der Sloot, H. A., A. van Zomeren, et al. (2003). Evaluation of environmental aspects of alternative materials using an integrated approach assisted by a database/expert system. Advances in Waste Management and Recycling. Dundee.

Velizarova, E., A. B. Ribeiro, et al. (2004). "Effect of different extracting solutions on the electrodialytic remediation of CCA-treated wood waste Part I.: Behaviour of Cu and Cr." Journal of Hazardous Materials **107**(3): 103.

Velizarova, E., A. B. Ribeiro, et al. (2002). "A comparative study on Cu, Cr and As removal from CCA-treated wood waste by dialytic and electrodialytic processes." Journal of Hazardous Materials **94**(2): 147.

Yu, K. and W. H. J. Patrick (2003). "Redox Range with Minimum Nitrous Oxide and Methane Production in a Rice Soil under Different pH." Soil Science Society of America **67**: 1952-1958.

Zhang, Y., Q. Liu, et al. (2001). "Sulfuric acid leaching of ocean manganese nodules using phenols as reducing agents." Minerals Engineering **14**(5): 525-537.